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CONTENTS

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Determination of Moisture by a High Frequency Titrator

Part I—Moisture in Ammonium Bicarbonate

By

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A method based upon the use of a high frequency titrator has been developed for the direct determination of moisture in ammonium bicarbonate. A suitable mixture of methanol and dioxan is added to solid ammonium bicarbonate samples containing different quantities of moisture—determined indirectly—and a standard curve is drawn by plotting the capacitance dial reading of the salt solvent system against moisture content in the salt. From the curve, the unknown moisture in a sample of ammonium bicarbonate can be determined.

Ever since the development of high frequency titrimetry by Jensen and Parrack[1] and independently by Balake[2], a number of analytical procedures have been developed based upon this technique. The advantages of this method lie in its relative accuracy, speed, simplicity and reproducibility. In this method of chemical analysis, a suitable cell containing the chemical system is made part of, or is coupled to, an oscillator circuit resonating at a frequency of several megacycles per second. With the changes in composition of the chemical system, the resistance (impedance) and/or capacitance of the circuit are altered, and changes are produced in oscillator characteristics, such as frequency, grid current and voltage and plate current and voltage. These changes are utilized in the analytical methods based upon high frequency titrimetry.

The present investigations were undertaken to apply this technique to the determination of moisture in salts, particularly in those cases where the usual methods are not satisfactory. Various direct and indirect electrical methods have been proposed[3–15] for the determination of moisture in solids, liquids and gases. Of these, some are specific for certain materials while those which are of a general nature involve the employment of complicated technique or of cumbersome equipment. The high frequency titrimetry, however, is a relatively simple technique and hence its application in moisture determination would be advantageous. West[11] et al have published a high frequency method for determining water in alcohols. Burton, Jensen and Kelly[16] have developed a high frequency method, using external electrodes, for the determination of moisture in sodium chloride and ammonium nitrate, in which the moist salt is stirred for 5 min. with an appropriate dioxane-methanol mixture and the current through the extract is measured. A good linear relation between current (microamperes) and moisture content was found for the range 0—2.1 per cent moisture.

A similar technique has been employed in the present investigations for the determination of moisture in ammonium bicarbonate for which no direct method was so far available.

Experimental

Apparatus: The apparatus used in these investigations is essentially the one developed by Hall[17] with certain modifications. It was selected particularly for its simplicity of operation and excellent time stability. It has a conductivity cell with no contact between the plates and solution, thereby removing many errors inherent in the usual conductivity cell.

The circuit used for this instrument is of crystal oscillator type with some modification[18], which has been used by Bender[19] and also by Fischer[20] for the determination of dielectric constant, and modified by Hall[17] (Fig. 1). An auxiliary vacuum tube voltmeter is required for following the effective overall conductance changes of the cell.

The principle of operation is simple. If the tuning capacitor of a crystal oscillator is set at a value too

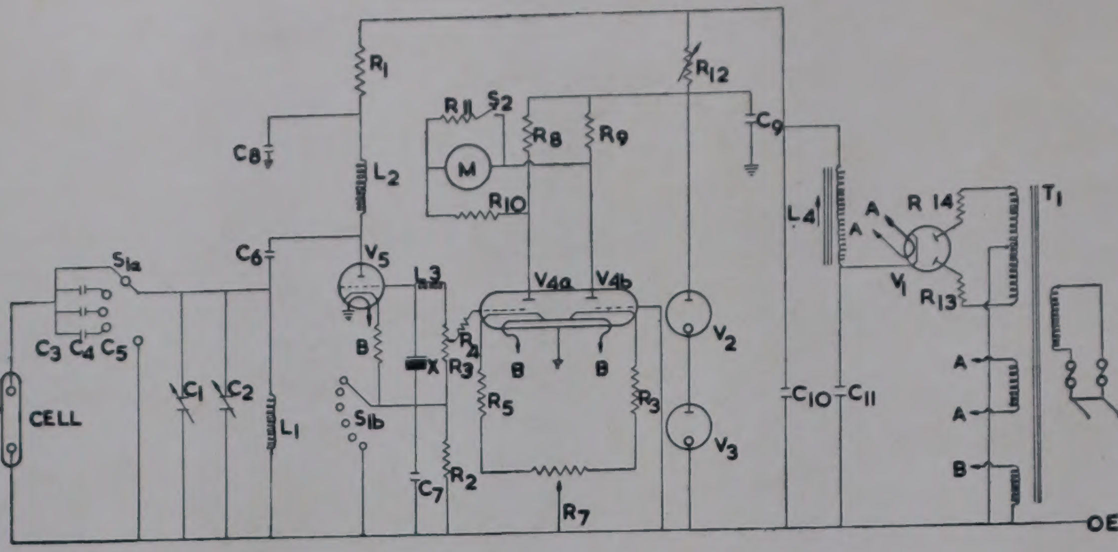

Fig 1—Circuit of High Frequency Titrimeter

C_1 = 100 $\mu\mu$F high stability standard variable condenser (Eddystone, Cat. No. 738) filled with vernier slow-motion dial (Eddystone)
C_2 = 27.5 $\mu\mu$ F high stability standard variable condenser (Eddystone Cat. No. 588) fitted with vernier slow-motion dial (Eddystone, Cat. No. 843)
C_3 = 27.5 $\mu\mu$ F high stability standard variable condenser (Eddystone, Cat. No. 588) fitted with vernier slow-motion dial (Eddystone, Cat. No. 843)
C_3 = 500 $\mu\mu$ F silvermica fixed condenser
C_4 = 200 $\mu\mu$ F do-
C_5 = 100 $\mu\mu$ F -do-
C_6 = 100 $\mu\mu$ F condenser
$C_7C_8C_9$ = 0.10 μ F condenser
$C_{10}C_{11}$ = 8 μ F electrolytic condenser, 450-volt D.C. working
R_1 = 33,000-ohm resistance
R_2 = 1,500-ohm high-stability resistance, 1 per cent tolerance.
R_3 = 33,000-ohm variable resistance
R_4 = 1 megohm resistances
R_5, R_6 = 2,200 ohm high-stability resistance, 1 per cent tolerance
R_7 = 1,000 ohm potentionmeter
R_8, R_9 = 30,000 ohm high-stability resistance, 1 per cent tolerance.
R_{10} = 820 ohm do- -do-
R_{11} = 47 ohm -do- -do
R_{12} = 20,000 ohm variable resistance
R_{13},R_{14} = 100-ohm resistance
L_1 = Turning Coil consisting of 50 turns of 26 gauge enamelled copper wire on a 1-in paxolin former.
L_2 = 2.5 millihenry radio frequency choke
L_3 = 13 millihenry frequency choke (Eddystone Cat. No. 1066)
V_1 = $5U_4$—GB rectifier
V_2, V_3 = $85A_2$ neon regulator
V_4 = ECC 81
V_5 = ECC 81 (only one-half used)
X = 2.4 megacycles per second crystal, 0.01 per cent (type 10X)
M = Moving Coil D.C. micrometer 0.250 A with mirror scale

great for oscillation to take place and then the capacitance is gradually decreased, a point is reached at which oscillation abruptly starts. This point may be precisely reproduced. This feature enables one to follow accurately the overall capacitance changes of a high frequency titration cell. If the tuning capacitor is adjusted until maximum resonant voltage is attained, the grid bias voltage is at a maximum. The maximum grid bias voltage at each point of a titration provides an excellent indication of effective conductance changes of the cell. The grid bias voltage may be measured by a vacuum tube voltmeter of a suitable range. Large changes of grid bias voltage are not directly proportional to conductance changes, but this does not interfere with the accuracy of the end-point determination.

The instrument has a circuit which gives a direct indication of both effective overall conductance and effective overall capacitance changes of a titration cell; these are read on a calibrated capacitor dial or on a valve voltmeter. The instrument has been assembled by Messrs Emission Radio and Varieties, Calcutta, on the basis of the circuit supplied to them (Fig. 1). It consists essentially of a crystal controlled oscillator—operating at 2.4 megacycles per second—in which the titration cell forms part of the tuned circuit, and a valve voltmeter. The change in meter (micro-ammeter) reading of the valve voltmeter is assumed to be proportional to the change in conductance of the titration cell at 2.4 Mc/s. Provision is also made for following the change in capacitance with the aid of two calibrated variable capacitors. A 5U4-GB valve (V_1) provides fullwave rectification from a transformer T through an inductance capacity filter giving a smooth high tension power supply for the oscillator. A regulated H.T. supply for the simple valve voltmeter is obtained across the two neon regulating tubes, V_2 and V_3. The current carried by V_2 and V_3 is adjusted by means of the variable resistance R_{12}. The resonant circuit of the

oscillator valve V_5 (double triode, half of ECC81) comprises the tuning coil L_1 the variable capacitors C_1 and C_2 and the titration cell. Some cells with particular solutions may give a high enough conductance component to dampen the oscillation completely. In such cases the switch and series capacitors—C_3, C_4 and C_5—may be used to bring the effective conductance within the range of the instrument. The frequency of oscillation is controlled by a quartz crystal, X, strapped between the control grid and cathode of the oscillator valve V_5. The negative bias voltage in the control grid of V_5 is developed across R_3 through the high frequency choke L_3.

The valve voltmeter is of the Wheatstone bridge type—the arms consisting of equal resistances R_8 and R_9 of 30,000 ohms each, while the other two formed by the internal resistances of valves V_{4a} and V_{4b} combined in a ECC 81 valve. The control grid of V_{4b} is earthed and that of V_{4a} is connected through a 1-megohm resistor R_4 to the slider of the sensitivity control R_3. Any voltage developed across the grid of V_{4a} will cause an unbalance in the circuit which will be detected in the micro-ammeter M. The micro-ammeter M is equipped with a shunt resistance R_{f1}, brought into the circuit by switch S_2 and thereby reducing the sensitivity. The valve voltmeter is balanced initially by switching S_1 to the earth position, whereupon the resonant circuit of the oscillator and R_2 are shorted to earth; with the sensitivity control R_3 set to zero and the meter at full sensitivity the preset potentiometer R_7 is adjusted to zero deflection on the meter. The titrimeter can be easily modified for use with frequencies up to 15 Mc/s. This merely involves introducing plug in type of quartz crystals of desired frequency and the corresponding plug in type coils.

Before being used, the instrument is put on long enough to permit the attainment of the temperature equilibrium, say for about 15 minutes. The solution under test is placed in the titration cell; the liquid level should be at least 1 cm. above the upper metal band. Oscillation is started by adjustment of C_1 and C_2. Depending upon the range, one of the condensers (main dial) is locked into position and the other one is rotated to give maximum deflection on the meter. The reading on the meter M is adjusted by means of the sensitivity control R_3 so that it does not exceed one-fifth of the full-scale deflection. The meter is then restored to full sensitivity by opening switch S_2 which has been closed until now and the condenser C_2 (IInd dial) is rotated to produce maximum deflection. For each reading, the only condenser C_2 is slowly turned until the meter reading is maximum; condenser C_1 is left in its original position during the whole of the experiment. The IInd dial reading recorded at each point is plotted to indicate the change of the effective overall capacitance of the cell. The maximum deflection reading of the meter (M) gives the overall conductance change and this can also be plotted.

The cell used in these experiments is of thin-walled borosilicate glass with aluminium sleeves fastened flush to the outside wall of the tube. Since the response is sensitive to change in position of the tube, it is mounted in a stand at a fixed position adjacent to the instrument.

Procedure

The basis of the experiments performed is similar to that described by Jensen[16] et. al with some modifications. Ammonium bicarbonate is not a very stable compound and even at ordinary temperatures it decomposes evolving ammonia and carbon dioxide. Hence the usual methods available for the determination of moisture in solids are not applicable in this case. Even Karl Fisher method could not be employed satisfactorily in this case. Studies were, therefore, initiated on the use of high frequency titrator for moisture determination in this substance. Attempts to determine directly the moisture in the solid failed as ammonium bicarbonate itself decomposes and no reproducibility of results is possible. So the most desirable method appeared to be to extract a weighed amount of the sample quickly with an appropriate solvent which does not react with it. While not all the moisture would be extracted from the moist sample by the solvent, the salt-solvent system would come to an equilibrium condition. With salt samples of higher moisture content the loading on the oscillator would be greater because of the higher content of moisture and salt in the solvent at the equilibrium condition. Because of the higher solubilities of water and salt when polar solvents are used, the loading effect tend to be great, thereby causing low response to change in moisture content, although the total response is high. On the other hand, when a non-polar solvent is used, only a small portion of salt and moisture is dissolved and total response is low. Therefore, a mixture of both polar and non-polar solvent system has to be selected to give an optimum loading on the instrument. The ideal solvent appeared to be one that would dissolve water well and yet dissolve the salt only enough to provide a solution with an appreciable but not excessive conductivity.

Methanol and 1-4 dioxan dissolve water well, but

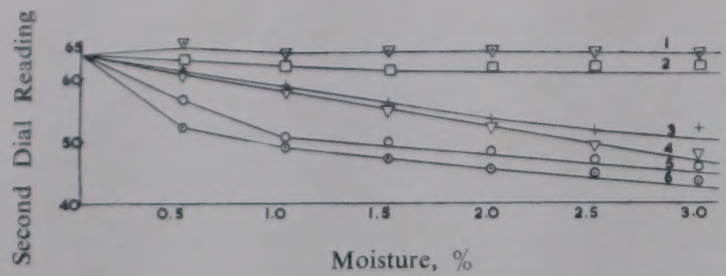

Fig. 2—Plot of Capacitance Dial Reading Against Moisture in Ammonium Bicarbonate with Different Proportions of Methanol and Dioxan by Volume.

1.	Methanol: dioxan	20:80
2.	-do-	40:60
3.	-do-	50:50
4.	-do-	55:45
5.	-do-	60:40
6.	-do-	20:80

dioxan does not dissolve ammonium bicarbonate at all, whereas methanol dissolves some amount of ammonium bicarbonate. So dioxan would give a very low response and methanol high response in the instrument with changes of moisture content in the salt. Various mixtures of methanol and 1-4 dioxan were tried. It would be seen that in case of ammonium bicarbonate, a mixture of 56 per cent by volume of methanol and 44 per cent by volume of dioxan gives best results (Fig. 2). This solvent composition is then the optimum for ammonium bicarbonate in this particular apparatus.

As ammonium bicarbonate is an unstable salt the time required for moisture determination should be kept as short as possible. So the solvent and salt mixture is stirred for the least time required for the supernatant liquid to give a constant current flow through the column; in this case the minimum stirring time is found to be 3 to 4 min. and which is maintained throughout at 4 min. In order to minimize the settling time after stirring, the stirred sample is centrifuged for 2 min. and the supernatant liquid is taken out. The stirring is done magnetically in a stoppered 100 ml. wide mouth Erlenmeyer flask.

The size of the sample tube is determined experimentally by trial and error until a tube is found which gives good response for very low percentage of moisture. In the present study a borosilicate glass tube of 15 mm. inside diam. and 1 mm. wall thickness is used; the length between the aluminium sleeves is 65 mm. The two aluminium sleeves are of 14 mm. width each. The zero set knob, the knob for the adjustment of magnitude of deflection in meter(M) and the condensce C_1 of main dial are kept in fixed positions throughout one series of experiments.

Temperature compensation is based on the premise that the predominant effect of a change of temperature would be due to the change in solubility of the salt and to the change in conductance of the ions in the solution. Thus, the change in the loading effect caused by the solvent itself over a given temperature range would be minor, in comparison with the change caused by the same solvent when it is saturated with dry salt. By adjusting initially the amplifier knob and the condenser C_1 in fixed position for the solvent saturated with dry salt, temperature control can be achieved. But in this particular case of ammonium bicarbonate one cannot get a completely dry sample. Hence, the initial reading was taken on a B.D.H. ammonium bicarbonate (L.R.) sample which was found to contain 0.48 per cent moisture as determined indirectly by analysis for all other ingredients.

20 g. of this sample was separately weighed out into different Erlenmeyer flasks and different quantities of moisture were added. Each sample was stirred for 4 min. with 50 ml. of methanol-dioxan mixture and then centrifuged for 2 min. The supernatant liquid was taken in the cell and the second capacitance dial reading noted each time corresponding to the maximum deflection in the meter M. The level of the liquid was kept 1 cm. above the upper strip each time. The second dial reading was plotted against the per cent moisture in the sample to get a standard curve. (Fig. 3). From this standard curve, the unknown moisture in a sample of ammonium bicarbonate can be estimated. The curve can be extrapolated to zero moisture, and from it moisture in samples having values less than 0.48 per cent can also be estimated. The meter (M) readings are not plotted as they do not give a linear relationship with the amount of moisture in the ammonium bicarbonate sample.

Results and Discussion

The moisture contents of various samples of ammonium bicarbonate (Table 1) as obtained from the plant in Sindri as also of an A.R. grade sample from Italy have been determinated by the new method. These results agree with those obtained by estimations of per cent ammonium bicarbonate, ammonium carbo-

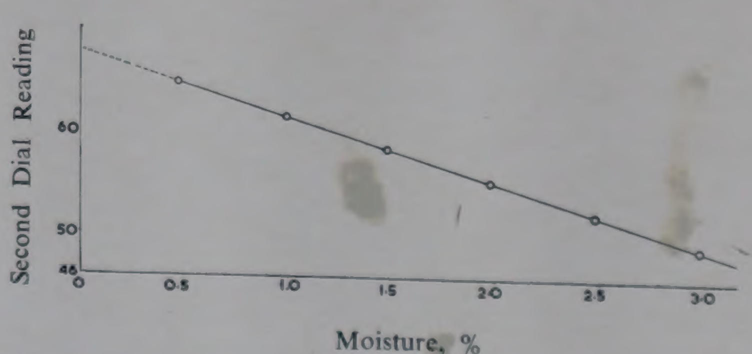

Fig. 3—Standard Curve for Moisture in Ammonium Bicarbonate

TABLE 1—MOISTURE DETERMINATION IN AMMONIUM BICARBONATE

Sample No.	Determined Indirectly, %	Determined by the Standard Curve: 2nd Dial Reading	Determined by the Standard Curve: Moisture, %
1 (B.D.H.; L.R.)	0.48	64.5	0.47
2	0.60	64.0	0.58
3	2.90	50.0	2.85
4	3.05	49.0	2.98
5 (Italian; A.R.)	0.41	65.3	0.39
6	0.69	63.5	0.66
7	1.61	57.5	1.64
8	1.05	61.5	1.01
9	2.61	51.0	2.65
10	2.96	49.5	2.90
11	1.30	60.0	1.26
12	1.81	56.5	1.78
13	2.41	52.5	2.45

nate and impurities in the samples and subtracting from 100. The standard curve gives correct results up to a total moisture content of 3 per cent. With higher moisture content the linear relationship is not obtained.

The high frequency apparatus has excellent time stability characteristics and results could be reproduced over extended period of time. Determinations can be made quite rapidly. With the initial gain already set, a single determination requires less than 10 min. including the time of stirring and centrifuging the salt-solvent systems. The method is, therefore, particularly suitable for quality control in the manufacture of ammonium bicarbonate.

Acknowledgement

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An Amperometric Method for the Estimation of Calcium Nitrate in Nitrophosphate and Calcium Ammonium Nitrate Fertilizers

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An amperometric method has been developed for the estimation of calcium nitrate in nitrophosphate and calcium ammonium nitrate. Calcium nitrate in the fertilizers is extracted by ammoniacal methyl alcohol (97 ml. methyl alcohol: 3 ml. of aqueous ammonia containing 0.134g./ml. NH_3), and the extract is titrated against a standard solution of sodium salt of EDTA using a zincate as the indicator ion.

Introduction

In an amperometric titration, change in the diffusion current of an electro-reducible ion in a given sample is noted, after each addition of the titrant, at a certain applied potential. The titration curve, which is a plot of this diffusion current versus the volume of titrant added, generally consists of two straight lines whose point of inter-section corresponds to the equivalence point.

The use of "polarographic indicators" for the detection of end-point in amperometric titrations was first suggested by Ringbom and Wilkman[1] particularly in those titrations in which neither the titrant nor the substance to be titrated yields a good diffusion current. They used Fe^{+++} ion as indicator ion for the titration of calcium and magnesium with fluoride and Cd^{++} ion for the titration of calcium against oxalate in 50 per cent ethanol. The indicator ion does not react during the course of titration, but it reacts with the excess of reagent in such a way that a sudden change in the polarographic current occurs at the end point.

Pribil and Vicenova[2] showed polarographically that zinc is quantitatively displaced from its complex with EDTA* by calcium ions in a 4N ammonium hydroxide solution. Laitenen et al[3] developed an amperometric method for the titration of calcium against disodium salt of EDTA with a zincate in potassium hydroxide as the indicator ion. Zincate has been used as indicator ion and its polarographic behaviour has been studied under different conditions.

The present investigation was undertaken to evolve an amperometric method for the estimation of calcium nitrate in nitrophosphate and calcium ammonium nitrate fertilizers. This estimation is important for quality control of the finished products. The method of Laitenen et al[3] has been applied with certain modifications in the present study.

Experimental

An Adept manually operated polarograph—model S—was used to obtain current voltage and amperometric titration curves. A fine capillary with a drop time (t) 4.5 sec. with open circuit and with the dropping electrode immersed in the solvent electrolyte was used (capillary characteristic $m^{2/3}\ t^{1/6}=1.84$). All polarographic studies and amperometric titrations were carried out in a H type cell of 100 ml. capacity. The second narrow arm was isolated from the broad one by a sintered disc and agar bridge. The cell circuit consisted of a staturated calomel electrode (S.C.E.), as reference agar bridge and a dropping mercury electrode. Nitrogen was bubbled through the cell for 1/2 hr. for complete deaeration before each experiment. Analytical grade mercury was used in the dropping

* Ethylene Diamine Tetraacetic acid

electrode. All the polarographic and amperometric studies were carried out at 25°C.

A 0.05N solution of disodium salt of ethelene diamine tetra-acetic acid (G.R.E. Merck quality) was used as a titrant solution and standardized against a standard calcium solution amperometrically.

The zincate indicator solution was prepared by dissolving 0.01M zinc oxide (Analar, B.D.H.) in a minimum amount of hydrochloric acid and adding 2M potassium hydroxide.

Ammonium nitrate (Analar, B.D.H.) used was dried in a vacuum oven at 50°C and a suction 20″ of Hg. Ammoniacal methyl alcohol was used to extract calcium nitrate from the fertilizers and synthetic mixtures. As pointed out in an earlier publication[4] this solvent quantitatively dissolves calcium nitrate in fertilizers leaving behind calcium carbonate. Subsequently, it has also been found that dicalcium phosphate and calcium sulphate also remain undissolved in this solvent.

Various mixtures were prepared from different analytical grade chemicals. A known amount of anhydrous calcium nitrate (AR, Poland) dissolved in methyl alcohol was added to each mixture. Mixtures were then dried and mixed thoroughly to make them homogeneous (Table 1). Different nitro-chalk samples were obtained from Nangal and Rourkela fertilizer works. Nitrophosphate samples were prepared in the laboratory by sulpho-nitric and carbo-nitric processes.

Calcium nitrate contents of the mixtures of nitro-chalk and nitrophosphate samples were also determined by the method described earlier[4].

The following experimental procedures were adopted for studying the polarographic behaviour of Zn^{2+} ion under different conditions.

(a) *Effect of Various Methyl Alcohol Media*: 10 ml. of zincate solution was taken in the cell to which 10, 20 and 30 ml. of methyl alcohol were added respectively. The volume of each solution was made up to 50 ml. Current-voltage curves drawn in each case are given in Fig. 1. Similar polarograms in 20, 40 and 60 per cent of ammoniacal methyl alcohol were also plotted.

(b) *Ammonium Nitrate as Supporting Electrolyte*: To 10 ml. of 0.01 M zinc solution 2.5, 12.5 and 25 ml. of 2M ammonium nitrate solution were added respectively. Each solution was diluted to 50 ml. and current-voltage

TABLE 1—COMPOSITION OF THE VARIOUS SYNTHETIC MIXTURES

Mixture No.	*Composition*
I	$CaCO_3$ (98%)+$Ca(NO_3)_2$ (1.93%)
II	$CaCO_3$ (59%)+NH_4NO_3 (40)%+ $Ca(NO_3)_2$ (0.8%)
III	$CaCO_3$ (35%)+$CaHPO_4$ (62.5%)+ $Ca(NO_3)_2$ (13.58%)
IV	$CaCO_3$ (25.55%)+$CaHPO_4$ (26.75%) +$Ca(NO_3)_2$ (2.42%)+NH_4NO_3 (45.7%)
V	$CaSO_4$ (25.5%)+$CaHPO_4$ (26.75%)+ $Ca(NO_3)_2$ (1.8%)+NH_4NO_3 (49.7%)

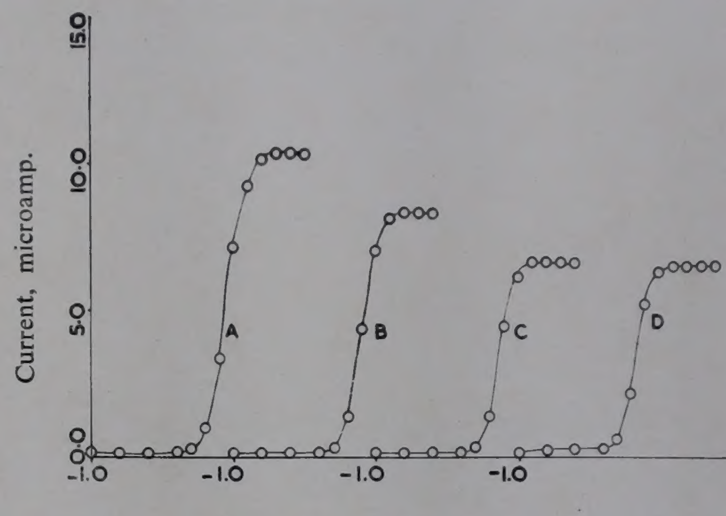

Fig. 1—Polarogram of Zn^{2+} Ion (.002 M) in Methyl Alcohol Medium 0.4 M KOH as Supporting Electrolyte

In A Water
B 20 % Methyl Alcohol
C 40 % -do-
D 60 % -do-

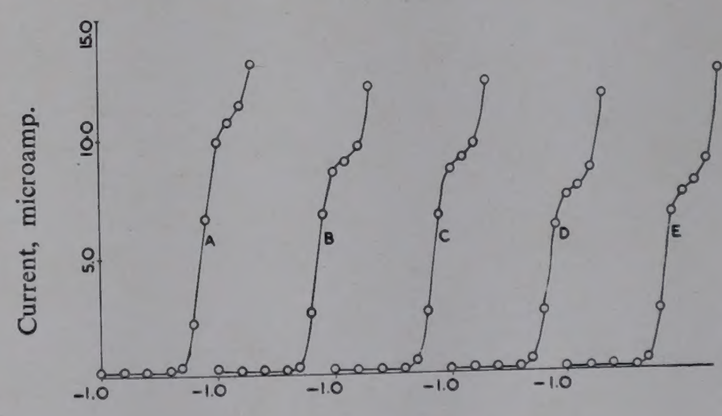

Fig 2—Polarogram of Zn^{2+} Ion (.002 M) in Mixed Electrolytes (0.4 M KOH + 0.1 M NH_4NO_3)

In A Water
B 20% Methyl Alcohol
C 20% Ammoniacal Methyl Alcohol
D 40% Methyl Alcohol
E 40% Ammoniacal Methyl Alcohol

curves in 0.1M, 0.5M and 1.0M ammonium nitrate were plotted.

(c) *Mixtures of Ammonium Nitrate and Potassium Hydroxide as Supporting Electrolyte, Methyl Alcohol and Ammoniacal Methyl Alcohol as Medium*: To a 10 ml. zincate solution in cell, 2.5 ml. of 2M ammonium nitrate, 10 and 20 ml. of methyl and ammoniacal methyl alcohol were added respectively. Each solution was made up to 50 ml. and polarograms were plotted (Fig. 2). Similar experiments were also repeated with 0.2M ammonium nitrate (Fig. 3).

(d) *Ammoniacal Methyl Alcohol Extract of Various Synthetic Mixtures and Fertilizers*: To a 10 or 20 ml. of the extract, 10 ml. of zincate solution was added and the solutions were diluted to 50 ml. The current-voltage curves were plotted (Figs. 4 & 5).

Ammoniacal methyl alcohol extracts of calcium ammonium nitrate, nitrophosphate and various mixtures

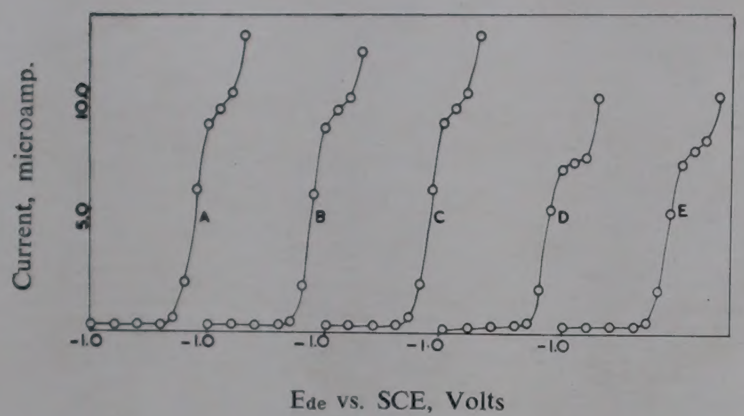

Fig 3—Polarogram of Zn^{2+} Ion (0.002 M) in Mixed Supporting Electrolytes (0.4 M KOH + 0.2 M NH_4NO_3)

In A Water
B 20% Methyl Alcohol
C 20% Ammoniacal Methyl Alcohol
D 40% Methyl Alcohol
E 40% Ammoniacal Methyl Alcohol

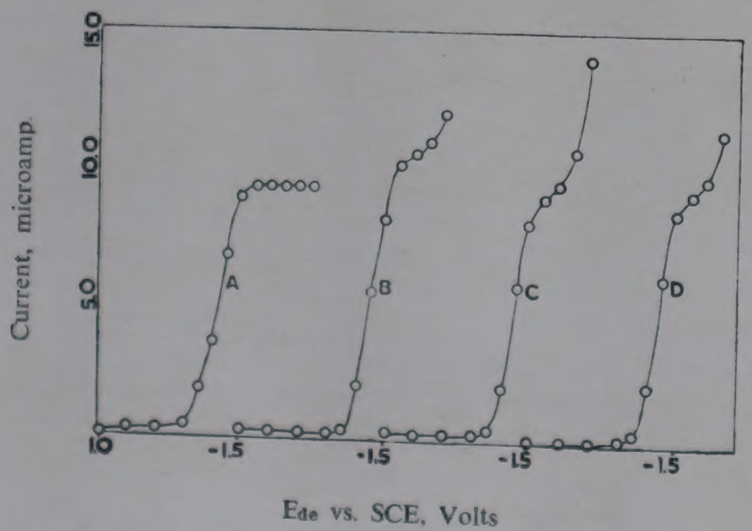

Fig. 4—Polarogram of Zn^{2+} Ion (0.002 M) in KOH and Ammoniacal Methyl Alcohol Extract (10%)

A $Ca(NO_3)_2$
B Mix. I containing 1.93% $Ca(NO_3)_2$
C Mix. II „ 0.78% „
D Nitro-Chalk „ 1.178% „

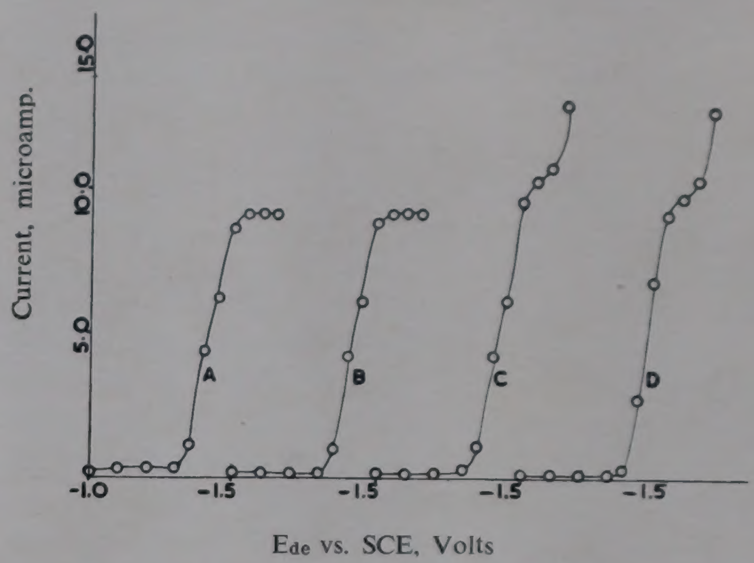

Fig. 5—Polarogram of Zn^{2+} Ion (0.002 M) + 0.4 M KOH + 10 ml. Ammoniacal Methyl Alcohol Extract

A Mix. III containing 3.83% $Ca(NO_3)_2$
B Mix. IV „ 2.38% „
C Mix. V containing 1.79% „
D Nitrophosphate containing 0.57% „

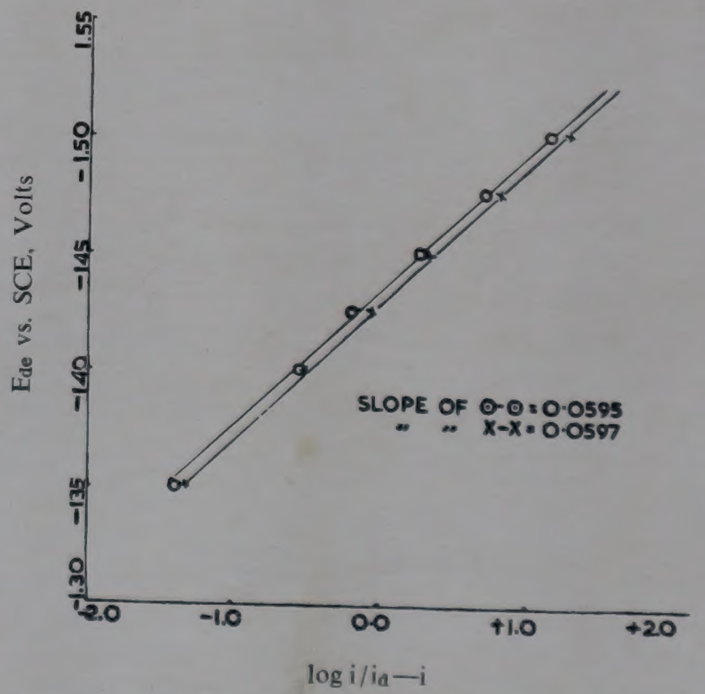

Fig. 6—Reversibility of Zn^{2+} Ion (0.002 M) + 0.4M KOH Supporting as Electrolyte

[Curves of similar nature were also obtained with Nitrochalk and Nitrophosphate Extracts]

O-O 0.1M $(NH_4)NO_3$ + 20% Ammoniacal Methyl Alcohol
X-X 0.1M $(NH_4)NO_3$ + 40% Ammoniacal Methyl Alcohol

were prepared by taking 5 to 10 g. of the substance and extracting it with ammoniacal methyl alcohol. The volumes of the extract were made up to 100 ml.

For performing amperometric titration the following procedure was adopted.

In a H cell, 10 or 20 ml. of ammoniacal methyl alcohol extract, depending upon the amount of calcium nitrate present in the fertilizer, was taken. To this, 10 ml. of zincate solution was added and the volume was made up to 50 ml. Nitrogen was bubbled for 1/2 hr. through the cell. A potential of -1.55 volts was applied corresponding to maximum diffusion current. A concentrated solution of sodium salt of EDTA was added in small increments with the help of a 2 ml. micro-burrette. The dilution effect was thereby avoided. Nitrogen was also bubbled for about 2 minutes after each addition of the titrant. The change in diffusion current after each addition of the titrant was noted and plotted against its volume. The intersection of two lines indicated the equivalence point. The different titration curves with various fertilizers and mixtures containing different amounts of calcium nitrate are shown in Figs. 7 and 8.

Results and Discussion

The ammoniacal methyl alcohol extracts of calcium ammonium nitrate and nitrophosphate contain mainly calcium nitrate and ammonium nitrate. The effect of various factors on the polarography of zincate in alcoholic medium is discussed below.

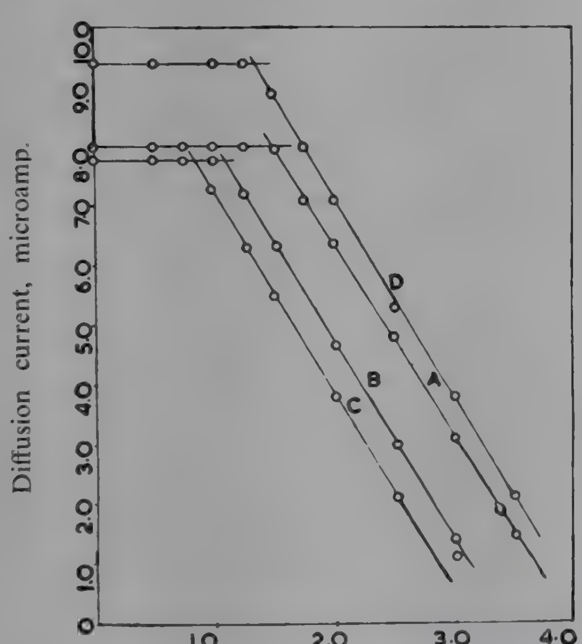

Fig. 7—Amperometric Titration of Ammoniacal Methyl Alcohol Extract of Various Synthetic Mixtures Containing 0.002 M Zn^{2+} as Indicator Ion in 0.4 M KOH

A A $Ca(NO_3)_2$ containing 3 mg. of Ca
B Mix. I containing 2.2 mg. of Ca
C Mix. II containing 1.6 mg. of Ca
D CAN Sample from Nangal containing 3.8 mg of Ca

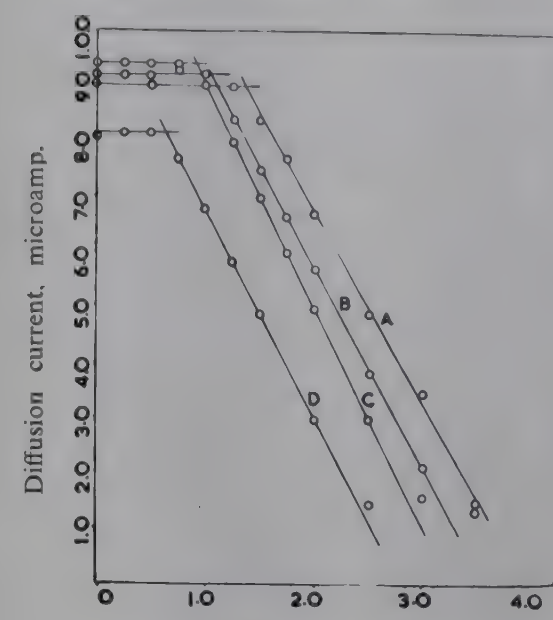

Fig. 8—Amperometric Titration of Ammoniacal Methyl Alcohol Extract of Various Synthetic Mixtures and Nitrophosphate Sample Containing 0.002 M Zn^{2+} in 0.4M KOH

A Mix. III containing 2.6 mg. of Ca
B Mix. IV containing 2.1 mg. of Ca
C Mix. V containing 3.6 mg. " "
D Nitrophosphate containing 1.2 mg. "

(a) *Effect of various methyl alcohol media*: From polarograms it is clear that the diffusion current of Zn^{2+} ion decreased with increasing amount of methyl alcohol in the medium (Fig. 1). The change was rapid up to a methyl alcohol content of 40 per cent. Similar effect has also been observed with ammoniacal methyl alcohol. The presence of ammonia does not affect the diffusion current of Zn^{2+} ion. From the knowledge of diffusion current and capillary characteristic, the value of diffusion current constant[5] can be calculated by $I = \frac{i_d}{C m^{2/3} t^{1/6}}$, where i_d is the diffusion current and C is the concentration in millimoles. The values of I and $E_{\frac{1}{2}}$ for above systems are given in Table 2. The reversibility of Zn^{2+} ion in ammoniacal methyl alcohol is tested by plotting the values of log $\frac{i}{i_d - i}$ vs potential applied. The plots are found to be straight lines with slopes 0.061, 0.060, 0.060 and 0.060 in water, 20, 40 and 60 per cent ammoniacal methyl alcohol respectively (Fig. 1).

TABLE 2

Supporting Electrolyte and Medium	$E_{\frac{1}{2}}$ vs. SCE, volts	I
(a) 0.002 M Zn^{2+}, 0.4 M KOH in pure H_2O	−1.46	2.79
(b) 0.002 M Zn^{2+}, 0.4 M KOH in 20% methyl alcohol.	−1.44	2.24
(c) 0.002 M Zn^{2+}, 0.4 M KOH in 40% methyl alcohol.	−1.43	1.78
(d) 0.002 M Zn^{2+}, 0.4 M KOH in 60% methyl alcohol	−1.41	1.74
(a) 0.002 M Zn^{2+}, 0.4 M KOH in 20% ammoniacal methyl alcohol	−1.44	2.22
(b) 0.002 M Zn^{2+}, 0.4 M KOH in 40% ammoniacal methyl alcohol.	−1.44	1.83
(c) 0.002 M Zn^{2+}, 0.4 M KOH in 60% ammoniacal methyl alcohol.	−1.43	1.78

TABLE 3—VALUES OF I & $E_{\frac{1}{2}}$ IN AMMONIUM NITRATE

Supporting Electrolyte and Medium	$E_{\frac{1}{2}}$ vs. SCE, volts	I
(a) 0.002 M Zn^{2+} in 0.1 M ammonium nitrate in H_2O.	1.01	2.79
(b) 0.002 M Zn^{2+} in 0.5 M ammonium nitrate in H_2O.	Ill-defined wave	—
(c) 0.002 M Zn^{2+} in 1.0 M ammonium nitrate in H_2O	Badly distorted wave	—

(b) *Ammonium Nitrate as Supporting Electrolytes*: Zn^{2+} ion gives two reduction waves at -0.95 and -1.15 volts respectively in 0.1M ammonium nitrate solution. Ill-defined waves are obtained in 0.5M and 1.0M ammonium nitrate. The values of $E_{\frac{1}{2}}$ and I in ammonium nitrate are given in Table 3.

(c) *Mixture of Ammonium Nitrate and Potassium Hydroxide as Supporting Electrolyte*: *Methyl Alcohol and Ammoniacal Methyl Alcohol as Media*: Polarograms of Zn^{2+} ion and 0.4M potassium hydroxide and 0.1M ammonium nitrate as mixed supporting electrolyte in various media consist of two reduction waves at potentials −1.35 and −1.60 volts (Fig. 2). The diffusion currents under these conditions are also found to be dependent on the amount of alcohol. Experiment with 0.2M ammonium nitrate and 0.4M potassium hydroxide also give polarograms of similar nature (Fig. 3).

(d) *Polarography of Zn^{2+} in Ammoniacal Methyl Alcohol Extract of Various Synthetic Mixtures and Fertilizers*: From Figs. 4 and 5, it is evident that the Zn^{2+} ion

TABLE 4—VALUES OF $E_{\frac{1}{2}}$ AND I IN MIXED SUPPORTING ELECTROLYTE I.E. NH_4NO_3+KOH

Supporting Electrolyte and Medium	$E_{\frac{1}{2}}$ vs. SCE, volts	I
(a) 0.002 M Zn^{2+}+0.4 M KOH+0.1 M NH_4NO_3 in pure water.	−1.44	2.43
(b) 0.002 M Zn^{2+}+0.4 M KOH+0.1 M NH_4NO_3 in 20% methyl alcohol.	−1.44	2.43
(c) 0.002 M Zn^{2+}+0.4 M KOH+0.1 M NH_4NO_3 in 20% ammoniacal methyl alcohol.	−1.44	2.43
(d) 0.002 M Zn^{2+}+0.4 M KOH+0.1 M NH_4NO_3 in 40% methyl alcohol.	−1.42	1.83
(e) 0.002 M Zn^{2+}+0.4 M KOH+0.1 M NH_4NO_3 in 40% ammoniacal methyl alcohol.	−1.43	1.93
(a) 0.002 M Zn^{2+}+0.4 M KOH+0.2 M NH_4NO_3 in H_2O	−1.45	2.87
(b) 0.002 M Zn^{2+}+0.4 M KOH+0.2 M NH_4NO_3 in 20% methyl alcohol.	−1.42	2.41
(c) 0.002 M Zn^{2+}+0.4 M KOH+0.2 M NH_4NO_3 in 20% ammoniacal methyl alcohol.	−1.42	2.43
(d) 0.002 M Zn^{2+}+0.4 M KOH+0.2 M NH_4NO_3 in 40% methyl alcohol.	−1.42	2.08
(e) 0.002 M Zn^{2+}+0.4 M KOH+0.2 M NH_4NO_3 in 40% ammoniacal methyl alcohol.	—142	2.16

gives the same nature of curve as in presence of ammonium nitrate (Fig. 3). For extract containing no ammonium nitrate, a single wave is obtained. The reduction potential are -1.35 and -1.60 volts vs. SCE for double waves and -1.35 volts for single wave. The values of $E_{\frac{1}{2}}$ and I for Zn^{2+} ion wave in various extracts are given in Table 5. Reversibility of Zn^{2+} ion in mixed electrolyte has also been studied. The plots of E_{de} vs SCE and log $\frac{i}{i_d - i}$ are found to be straight lines with slopes 0.0595, 0.0597, 0.595 and 0.595 under various conditions showing the systems to be reversible (Fig. 6).

From polargraphic studies of Zn^{2+} ion with respect to the composition of ammoniacal methyl alcohol extract of nitro-chalk and nitrophosphate fertilizers, it is concluded that zinc ion gives two reduction waves. The $E_{\frac{1}{2}}$ values are found to be between −1.42 to −1.45 under various conditions. The value of $E_{\frac{1}{2}}$ for Zn^{2+} ion in 1M sodium hydroxide is reported to be -1.53 volts. So the amperometric titrations in ammoniacal methyl alcohol are possible at the potential correspond-

TABLE 5—VALUES OF $E_{\frac{1}{2}}$ AND I OF Zn WAVE IN THE ALCOHOLIC EXTRACT OF VARIOUS SYNTHETIC MIXTURES OF NITRO-CHALK AND NITROPHOSPHATE SAMPLES

Supporting Electrolyte and Medium	*$E_{\frac{1}{2}}$ vs. SCE, volts*	*I*
(a) 0.002 M Zn^{2+}+0.4 M KOH+$Ca(NO_3)$ alone, extract containing no ammonium nitrate.	−1.42	2 43
(b) 0.002 M Zn^{2+}+0.4 M KOH+10 ml. ammoniacal methyl alcohol extract of Mix. I.	−1.42	2.43
(c) 0.002 M Zn^{2+}+0.4 M KOH+10 ml. ammoniacal methyl alcohol extract of Mix. II.	−1.43	2.73
(d) 0.002 M Zn^{2+}+0.4 M KOH+10 ml. ammoniacal methyl alcohol extract of of Nitrochlak.	−1.43	2.57
(a) 0.002 M Zn^{2+}+0.4 M KOH+10 ml. ammoniacal methyl alcohol extract of of Mix. III.	−1.41	2.30
(b) 0.002 M Zn^{2+}+0.4 M KOH+10 ml. extract of Mix. IV.	−1.44	2.62
(c) 0.002 M Zn^{2+}+0.4 M KOH+10 ml. extract of Mix. V.	−1.43	2.22
(d) 0.002 M Zn^{2+}+0.4 M KOH+10 ml. extract of the nitrophosphate.	−1.44	2.27

ing to maximum diffusion current of the lst wave i.e. -1.55 volts.

The reason for the choice of zincate as indicator ion for the amperometric determination of calcium has already been explained by Laitenen[3] et al. They found Zn^{2+} ion as most suitable for the titration of calcium on the basis of formation constants of Zn-EDTA and Ca-EDTA complexes, which are 7.1×10^{-17} and 2.6×10^{-11} respectively according to Swarzenbach[7]. Sodium salt of EDTA first reacts with calcium to form a complex and until all calcium is titrated, there is no change in the diffusion current. After that a sudden change in the diffusion current of Zn^{2+} ion is observed due to formation of Zn-EDTA complex.

Calcium nitrate is titrated in various extracts and the variation of diffusion current is plotted against volume of sodium salt of EDTA added. The plots (Figs. 7 and 8) show straight portions due to formation of Ca-EDTA complex with sudden change at the equivalence point. The equivalence points directly indicate the volume of sodium salt of EDTA consumed. Calcium nitrate content is calculated according to following equation: $\% \ Ca(NO_3)_2 = \frac{164.4 \times V \times N}{W}$ for 10 ml. extract taken and $\frac{82.2 \times V \times N}{W}$ for 20 ml. extract, where V is the volume of the titrant and N is its normality and W is the weight of sample taken. The results of estimations of calcium nitrate by the amperometric method in different samples of fertilizers and synthetic mixtures are given in Tables 6 and 7. Estimations were also carefully carried out by the permanganate method[4] using ammoniacal methyl alcohol

TABLE 6—CALCIUM NITRATE CONTENT OF VARIOUS SYNTHETIC MIXTURES

Mixture	*Applied voltage E_{de} vs. SCE*	*Media*	*Calcium Nitrate Content by Permanganate Method, %*	*Average Calcium Nitrate Content by Amperometry, %*	*Standard Deviation*
$Ca(NO_3)_2$ alone	−1.55 volts	20% methyl alcohol	0.25	0.25	0.00
$CaCO_3+Ca(NO_3)_2$	−1.55 volts	20% ammoniacal methyl alcohol	1.92	1.93	0.01
$CaCO_3+Ca(NO_3)_2+NH_4NO_3$	−1.55 volts	20% ammoniacal methyl alcohol	0.77	0.78	0.01
$CaHPO_4+CaCO_3+Ca(NO_3)_2$	−1.60 volts	20% methyl alcohol	3.58	3.57	0.01
$CaCO_3+Ca(NO_3)_2+CaHPO_4+NH_4NO_3$	−1.60 volts	20% ammoniacal methyl alcohol	2.39	2.40	0.02
$CaSO_4+CaHPO_4+Ca(NO_3)_2+NH_4NO_3$	−1.60 volts	20% ammoniacal methyl alcohol	1.81	1.79	0.02

TABLE 7—CALCIUM NITRATE CONTENT OF VARIOUS SAMPLES OF CALCIUM AMMONIUM NITRATE AND NITROPHOSPHATE

Calcium Ammonium Nitrate						Nitrophosphate					
Sample	*Applied voltage E_{de} vs. SCE*	*Media*	*Calcium nitrate content by Permanganate method, %*	*Average calcium nitrate by Amperometry, %*	*Standard deviation*	*Sample*	*Applied voltage E_{de} vs. SCE*	*Media*	*Calcium nitrate content by Permanganate method, %*	*Average nitrate content by Amperometry, %*	*Standard deviation*
a	−1.55 V	20% ammoniacal methyl alcohol	1.17	1.18	0.01	A	−1.60 V	20% ammoniacal methyl alcohol	0.57	0.58	0.01
b	,,	,,	0.52	0.50	0.02	B	,,	,,	9.33	9.25	0.13
c	,,	,,	0.68	0.65	0.03	C	,,	,,	0.19	0.18	0.01
d	,,	,,	0.62	0.60	0.02	D	,,	,,	nil	nil	—
e	,,	,,	0.55	0.54	0.01	E	,,	,,	nil	nil	—
f	,,	,,	0.53	0.52	0.01						

as the extracting medium. The experimental data show that the amperometric method is precise and has the same degree of accuracy as the volumetric method involving the use of standard potassium permanganate (Table 6 & 7).

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A Spectrographic Study of Trace Elements in Some Indian Soils

By

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Some Indian soils have been analysed by emission spectrography for trace elements which influence the nutrition of plant, and among them the following have been estimated: gallium, nickel, chromium, vanadium and manganese. For these elements, molybdenum was found to be a suitable internal standard.

Introduction

It is well-known that fertilizers react with soil in a very complex manner, and besides the nitrogenous, phosphatic and potash fertilizers some micro-nutrients also play a vital role in the metabolism of plants and animals. Copper deficiency in soil has been shown by Beeson[1] to cause malnutrition in animals. The importance of an essential micro-nutrient like manganese has been shown by a number of workers, and Pirson[2] has discussed its role in photosynthesis. Nason[3] has described the metabolic role of molybdenum and vanadium in plants and animals, while the metabolic roles of zinc and cobalt have been discussed by Hoch[4] and by Davis[5] respectively. The importance of boron has been discussed in detail by many workers including Skok[6] and vanadium has been shown to be a micronutrient for species like green algae.[7]

As such, it will be interesting to make a rapid survey of the distribution of these trace elements in soils of the different regions of our country. Keeping this object in view, some representative soils have been tested by spectrochemical method to get an idea of the nature of the elements present in each and the concentration of a few trace elements, viz. Ga, Ni, Cr, V and Mn in them.

For the latter problem, various internal standards have been used by different workers. Mitchell[8] used molybdenum as an internal standard for the estimation of silicon, aluminium, potassium, iron, calcium and magnesium, while Lakanen[9] used indium and palladium for nickel, chromium, vanadium, gallium and a few others. Molybdenum has been used satisfactorily as an internal standard in the present investigation.

Experimental

Equipments: The following equipments have been used:

Spectrograph: KCA-1 glass/quartz spectrograph having a linear dispersion of 4.6 Å/mm at 3000 Å for quartz optics (Russian make).

Power Unit: D.C. power supply (Indian make) giving an output of 110 volts and current upto 10 amperes.

Microphotometer: Reading/recording microphotometer model MF-4 (Russian make).

Electrodes: Pure graphite rods from Messrs Johnson and Matthey were used for electrodes. Lower electrode (anode) was 2 cm. long with 6 mm. external and 3 mm. internal diameter. The crater was 3.5 mm. deep. Upper one was 2 cm. long and 6 mm. in diameter with a conical end.

Procedure

Soil Samples: The seven representative samples of surface soil taken for the present study were from (1) Amraoti (Maharashtra) (2) Jodhpur (Rajasthan), (3) Ludhiana (Punjab), (4) New Delhi, (5) Sindri (Farm), (6) Sindri (Rangamati area) and (7) Chaibasa (Bihar), of which the first four are alkaline having pH as 8.3, 8.3, 8.45 and 7.7 respectively. The two Sindri samples are neutral to slightly acidic having pH 6.9 and 6.65 respectively, while the Chaibasa soil is almost neutral[10].

0.5 g. of finely ground and oven-dried sample was ignited at 450°C to destroy the organic matter in it which may suppress the emission of spectral lines.

A. Qualitative Analysis

About 50 mg. of each of the above samples were mixed thoroughly with equal amount of pure graphite powder, and about 25 mg. of each of the mixtures was filled in duplicate graphite electrodes, which were used as anodes for two spectral regions (2450-3350 Å and 3000-5000 Å), photographed for qualitative work.

The slit of the spectrograph was kept 0.01 mm. wide, and samples were arced at 9 amp. for 60 seconds. Iron spectra were recorded on the same plate for identification of lines. Agfa ultraviolet plate used was processed in the usual way. The elements were identified visually and are tabulated wherein an idea about order of their concentration has been furnished (Table 3).

B. Quantitative Analysis

(1) *Test Samples*: A buffer of graphite powder with 2.5 per cent of pure MoO_3 (internal standard) was prepared. 50 mg. of soil sample (prepared above) was thoroughly mixed with equal amount of buffer and 20 mg. of this admixture was filled in the crater of the anode. In a similar way other test samples were prepared and packed in electrodes.

(2) *Synthetic Standards*: A suitable soil base was prepared by mixing together very pure samples of SiO_2 73.5, Al_2O_3 10.0, Fe_2O_3 5.0, $CaCO_3$ 3.5, MgO 1.5, Na_2CO_3 3.0, K_2SO_4 2.5 and TiO_2 1.0 per cent and sintering overnight at 1250°C. The percentage compositions of these salts are so chosen that the base composition approaches the average composition of most of the soils under investigation.

A mixture of trace elements—mostly in oxide form—was prepared. A set of five standards was made by mixing different amounts of this mixture with the soil base. A second power increase in the concentration of trace elements has been used. Their concentrations in the synthetic standards are shown in Table 1.

50 mg. of each standard was mixed with an equal amount of buffer containing internal standard, and 20 mg. of this admixture was packed in the anode of graphite electrode for arcing.

(3) *Production of Spectra:* Spectral region was set for 2600 to 3700 Å. The slit width was fixed at 0.01 mm., and the arc was run at low current for 5 secs. The current was then raised to 9 amp. and a total exposure of 60 secs. was given on Agfa ultraviolet (9×24 cm.) plate. Both, the soil samples and synthetic standards were recorded on the same plate. An iron spectrum was also recorded beside these.

For quantitative work microphotometric readings were noted for analytical pair of lines of Mo and the element to be estimated. Selected analytical lines are given in Table 2. Working curves were drawn between logarithm of concentration of particular element and

TABLE 1—CONCENTRATION OF TRACE ELEMENTS IN SYNTHETIC STANDARDS, PPM

Standard Number	*Ga*	*Ni*	*Cr*	*V*	*Mn*
I	119	306	437	493	12,480
II	60	153	219	247	6,240
III	30	77	109	123	3,120
IV	15	38	55	62	1,560
V	7	19	27	31	780

TABLE 2—SELECTED ANALYTICAL LINES

Trace Element	*Wave Length, Å*	*Internal Standard, Å*
Ga	2943.637	Mo 2930.503
Ni	3050.819	Mo 3112.124
Cr	3014.915	Mo 2930.503
V	3185.396	Mo 3208.834
Mn	2933..063	Mo 2930.503

TABLE 3—QUALITATIVE ANALYSIS OF THE SOIL SAMPLES (*Visual Inspection*)

Sl No.	*Description*	*Elements Detected*
1.	Amraoti Black Cotton Soil	Si, Al, Fe, Ca, Mg, Ti, K, Na, Mn, Cr, V, Ni, Cu, Ba, Sr and Ga.
2.	Jodhpur Sandy Soil	Si, Al, Fe, Ca, Na, K, Mg, Mn, Ti, Cr, V, Ni, Cu, Ga, Sr, Ba and Ag.
3.	Ludhiana Soil	Si, Al, Fe, Ca, Na, K, Mg, Mn, Ti, Cr, V, Ni, Cu, Ba, Ga, Sn and Pb.
4.	New Delhi Soil	Si, Al, Fe, Ca, Na, K, Mg, Mn, Ti, Cr, V, Ni, Cu, Ba, Ga and Pb.
5.	Sindri Farm Soil	Si, Al, Fe, Ca, K, Na, Mg, Mn, Ti, Cr, V, Ni, Cu, Ba, Ga and Pb.
6.	Sindri Red Soil	Si, Al, Fe, Ca, K, Ti, Na, Mg, Cr, V, Mn, Ni, Cu, Ba, Ga and Pb.
7.	Chaibasa Soil	Si, Al, Fe, Ca, K, Na, Mg, Mn, Ti, Cr, V, Ni, Cu, Ba, Ga and Sr.

N.B. Amounts roughly in decreasing order.

TABLE 4—TOTAL CONTENT OF TRACE ELEMENTS IN SOME INDIAN SOILS, PPM IN AIR-DRY SOIL

Sl. No.	*Description*	*Ga*	*Ni*	*Cr*	*V*	*Mn*
1.	Amraoti Black Cotton Soil	23	48	115	227	1,253
2.	Jodhpur Sandy Soil	15	30	104	58	517
3.	Ludhiana Soil	36	53	126	111	814
4.	New Delhi Soil	18	47	132	83	588
5.	Sindri Farm Soil	17	63	109	95	447
6.	Sindri Red Soil	30	35	155	178	552
7.	Chaibasa Soil	28	82	176	346	654

logarithm of ratio of galvanometric deflections for the analytical pair. From the curves, the amounts of elements in soils were noted (Table 4). The results are on oven dry weight basis.

Discussion

In the list of elements present in soils (Table 3) the spectral lines of some of the elements like lead (present in sample Nos. 3, 4, 5 and 6), tin (in No. 3) and silver (in No. 2) are found to be very faint due to their very low concentration and cannot be measured accurately with microphotometer. Again, the sensitive lines of strontium (4607.33 Å) and barium (4554.04 Å) do not fall in the region under investigation for quantitative work. However, their presence in soil samples (Sr in sample No. 1, 2 and 7 and Ba in all samples) has been established from their above lines in the region of 3000-5000Å which was photographed along with the region of 2450-3400Å for qualitative work. Copper was found to be present in all the samples but due to its very low concentration, only two of its most sensitive lines (3247.54 and 3273.96 Å) could be detected. But these lines interfere with manganese and titanium—present in soils—lines, and therefore it could not be estimated.

Other elements of interest like molybdenum, cobalt, zinc and boron were not found in these soil samples. For detection of boron, copper electrodes were used. It is believed that their amounts in samples under consideration are below the detection limit of the present experimental condition and/or intensities of their spectral lines have been suppressed. In connection with the latter, there are already some interesting references in the literature. Brode[11] studied the effect of large amounts of iron on the suppression of sensitivity of the boron lines. Scott[12] found that intensity of zinc line was greatly suppressed by sodium chloride and that of molybdenum by silica. He also found that intensity of cobalt line was greatly depressed by sodium carbonate.

From Table 4, it is seen that the amount of manganese varies from 447 ppm. (in Sindri farm soil) to 1,253 ppm. (in Amraoti black cotton soil). The amount of manganese in Amraoti soil appears to be high but manganese as high as 1210 ppm. has been reported in certain Bihar soils[13]. Also, it may be mentioned that 814 ppm. manganese in Ludhiana soil found by us is higher than 546 ppm. found by chemical analysis[14]. This variation may be alone due to usual soil variation.

The amount of vanadium varies from 58 ppm. in Jodhpur sandy soil to 346 ppm. in Chaibasa soil. Its role is important as it can substitute for molybdenum. Nickel varies from 30 ppm. in Jodhpur sandy soil to 82 ppm. in Chaibasa soil, while chromium from 104 ppm. in Jodhpur sandy soil to 176 ppm. in Chaibasa sample and gallium from 15 ppm. in Jodhpur sandy soil to 36 ppm. in Ludhiana soil. It is generally found that the trace elements are minimum in sandy soils.

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Studies on Some Indian Limestones Part II—Estimation of Dolomite A: Differential Thermal Analysis

By

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Attempts have been made to determine dolomite in Indian limestones by differential thermal analysis.

Introduction

In our previous communication[1], the mineralogical composition of some Indian limestone samples which are used as diluent for the manufacture of calcium ammonium nitrate (CAN) has been reported. Since dolomite ($MgCO_3$. $CaCO_3$) was found to be one of the constituents in those samples and its association with CAN is useful due to its poor aptitude for reacting with ammonium nitrate[2], as such a knowledge of its content in limestone is of vital importance so far as their utilisation as diluent for CAN is concerned.

For the estimation of dolomite some physical methods like x-ray diffraction[3] and differential thermal analysis[4], have been utilized. For estimation by the differential thermal analysis, maintenance of CO_2 atmosphere in the furnace is necessary. By this method, dolomite content as low as 0.3 per cent, where x-ray diffraction technique fails even to detect[4], has been determined. For the maintenance of a controlled atmosphere in the furnace, a DTA apparatus of complicated design is required. Attempts have, therefore, been made to find out whether dolomite in some Indian limestones can be estimated in the ordinary atmosphere using a simple apparatus capable of fabrication locally. Further, these results have been compared with those obtained in CO_2 atmosphere.

Experimental

The samples used in this investigation were the same reported in our previous communication[1]. The known mixtures of Jharbeda limestone and Rishikesh dolomite were used for making the calibration curve drawn with the percentages of dolomite vs. peak areas (Fig. 1).

The DTA instrument was of Linseis model and fully automatic. The thermocouple was of Pt/Pt-Rh, and the sample holders were of thin platinum cylinder. The rate of heating was controlled at 10°C/min. by a programme controller. Ignited alumina was used as a reference substance, and the amount of substance filled in the sample holder for each experiment was 1.50 g. The experiments were performed by maintaining CO_2 atmosphere in furnace as well as in ordinary atmosphere. It was observed that the other minor constituents present do not interfere with the characteristic endothermic peak of dolomite, which appears at 800°C[1]. This peak temperature is also unaffected by the furnace atmosphere[5]. For the estimation of dolomite, this peak was therefore chosen and closed by drawing a straight line touching the curvature sides of the peak,

A—in ordinary atmosphere; B—in CO_2 atmosphere

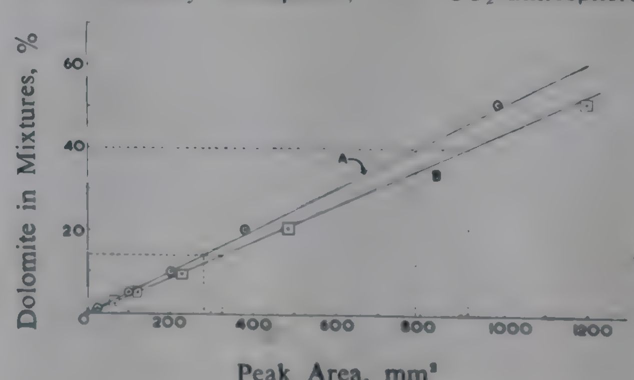
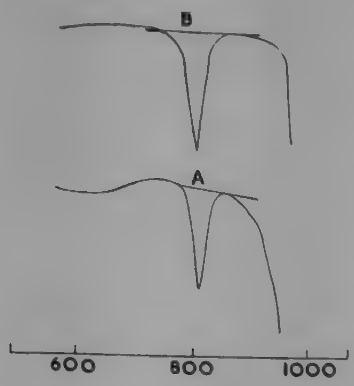


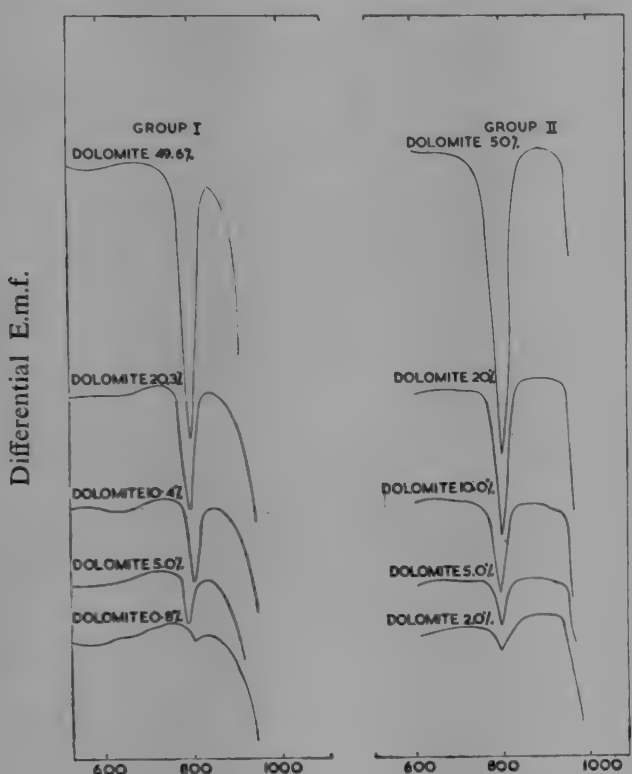
Fig. 1—Calibration Curve Prepared from Synthetic Mixtures of Jharbeda Limestone and Rishikesh Dolomite

A—in ordinary atmosphere; B—in CO_2 atmosphere



Temp., ° C

Fig. 2—DTA Thermograms of a Synthetic Mixture of Limestone and Dolomite



Temp., ° C

Fig. 3—DTA Thermograms of Synthetic Mixtures of Jharbeda Limestone and Rishikesh Dolomite

Group I—in ordinary atmosphere

Group II—in CO_2 atmosphere

and the area enclosed therein was measured (Fig. 2).

Dolomite in prepared mixtures of Punjab limestone and Rishikesh dolomite was also determined at ordinary atmosphere, and results were compared with the calculated value (Table 2).

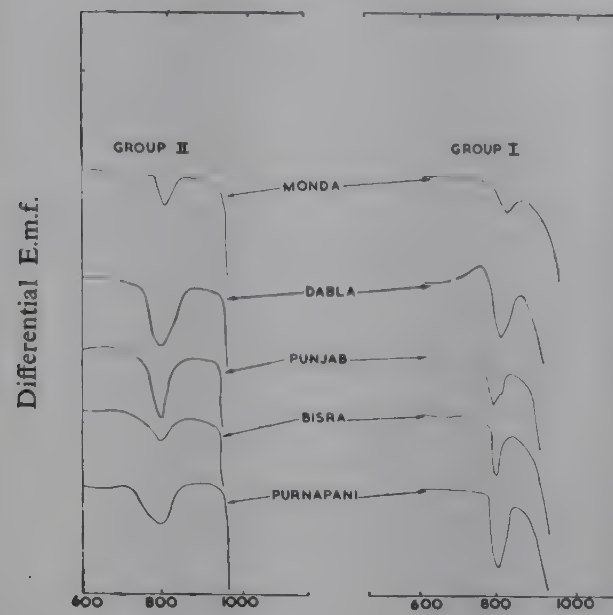
The results are shown in Table 1 and the DTA thermograms, viz. Figs 3 and 4.

Discussions

The results indicate that the amount of dolomite in the test samples are within 4.4-13 per cent, and that the

Group I—in ordinary atmosphere

Group II—in CO_2 atmosphere



Temp., ° C

Fig. 4—DTA Thermograms of Limestone Samples

TABLE—1—Dolomite Content in Limestone Samples

Sample	*Dolomite From the Peak Area,%*	
	Using ordinary atmosphere	*Using CO_2 atmosphere*
Monda	4.4	4.3
Dabla	13.0	12.8
Punjab	7.2	7.4
Bisra	6.2	6.0
Purnapani	11.0	11.2

TABLE 2—Dolomite Contents in the Prepared Mixtures of Punjab Limestone-Rishikesh Dolomite, %

Calculated	*From Peak Area*
7.2	7.2
7.6	7.7
8.3	8.3
16.2	16.0
30.2	30.2

results obtained in ordinary furnace atmosphere agree well with those obtained by using CO_2 atmosphere (Table 1). But it has been observed that for a given concentration of dolomite in a sample, the peak area obtained by using CO_2 atmosphere is higher than that at ordinary atmosphere (Fig. 1). This can be explained from the DTA curves of the prepared mixtures of limestone and dolomite samples as well as those of the test samples (Fig. 3 and 4).

Unlike in the CO_2 atmosphere, the peak of dolomite at 800°C does not return to base line in ordinary atmosphere, and the end of this peak is immediately followed by the second peak which is due to decomposition of calcium carbonate. Evidently this deviation is proportional to the difference of the peak areas obtained by using CO_2 as well as ordinary atmosphere. Again it is evident from the nature of their calibration curves that this difference of peak areas increases uniformly with increase of dolomite content (Fig. 1). This uniformity may be due to the use of large quantity (1.5 g.) of sample which on decomposition around 800°C evolves appreciable amount of CO_2 inside the furnace, thus maintaining an atmosphere that minimizes the base line shift and therefore results in minimum scattering of peak areas in the calibration curve. That is why estimation of dolomite is possible in ordinary atmosphere.

The validity of this method was also checked by using known mixtures of dolomite and a limestone which is different from that used for calibration curve. The results show that percentage of dolomite obtained by this method agrees well with the calculated values.

It is worthwhile mentioning here that dolomit content as low as 0.5 per cent has been detected in prepared mixture, and can therefore be estimated by this method.

Acknowledgement

The authors' thanks are due to Dr. K. R. Chakravorty, General Manager, Planning and Development Division, for his encouragement and keen interest in the problem and for permission to publish this paper. Thanks are also due to Mr. R. Jayaraman, Addl. Superintendent, for encouragement, and to Dr. B. K. Banerjee, Deputy Supdt., for his helpful suggestions and discussions during the course of this investigation.

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Studies on Some Indian Limestones Part II—Estimation of Dolomite B: X-Ray Method

By

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An attempt has been made to develop a method for the estimation of dolomite in some Indian limestones. It has been shown that dolomite can be estimated directly, and other minerals, particularly calcite, do not interfere up to the concentration range studied.

Introduction

The mineralogical investigation[1] on some Indian limestones, used as diluent in the manufacture of calcium ammonium nitrate (CAN), revealed that they contain dolomite ($MgCO_3.CaCO_3$) and also one per cent of magnesium carbonate. Such dolomitic limestones have potentialities in industrial and agronomical purposes. Their association with CAN is advantageous because of its poor reactivity with ammonium nitrate[3] and nutritional value for the plants. While the conventional chemical methods of analysis are time-consuming and require sufficient skill they are not capable of revealing any information on the crystalline form and state of aggregation. In view of this, an attempt has

been made to develop a method for the estimation of dolomite in limestone by x-ray diffraction method.

Experimental

Description of the Method: In case of X-ray diffraction method, the quantitative method is based upon the fact that the intensity of a diffraction line of a substance, characteristic of which is under consideration, depends on the concentration of that substance in the mixture. The intensity of the diffraction line can be measured from its peak height or area (integrated intensity). The method of analysis can be broadly classified into the following: (i) Direct and (ii) internal standard techniques.

Gulbrandsen[3] attempted to determine the ratio of calcite to dolomite in carbonate rocks by x-ray method using different types of background mixtures composed of different minerals. In the present case, the attempt has been to use a direct method of analysis to determine dolomite absolutely. The internal standard technique is valid only if the various elements in the matrix of the sample affect the reference and the analytical lines exactly the same way. Moreover, the most important requirements of elements used as reference standards are their availability, absence of the reference element in the sample and many other factors. So, the direct method has the advantage over the internal standard technique in the matter that it is simple, less time-consuming and that it does not depend on the availability of reference standard, which is very important, so long there is no matrix absorption and interferences due to other elements.

Procedure: Six different samples of limestone and one of dolomite, collected from Nangal (Punjab) and Rourkela (Orissa) fertilizer factories, were used in the present investigation. The materials were finely ground, dried and stored in a desiccator.

Philips X-ray diffractometer PW 1050/51, with Geiger Counter as detector, was used for the quantitative analyses. Filtered Cu K_α radiation with nickel filter was used. A strip chart was run up to 20-40° at a scanning speed 1°/min. with time constant 2 secs in order to check the interference and to select the locations for background measurement. The background was measured at a 2θ position slightly larger than that for the dolomite line used. The intensities of the lines were determined from Geiger counts by setting the Geiger tube position manually at the desired angle. The operating conditions for the diffractometer were as follows: X-ray tube 40 KV, 20 mA; Multiplication 1; Detector Geiger Muller counter tube 1650 V; Scale selector 8; Time constant 2 secs; Scatter slit 1°; Receiving slit 0.2 mm. and Divergence slit 1°.

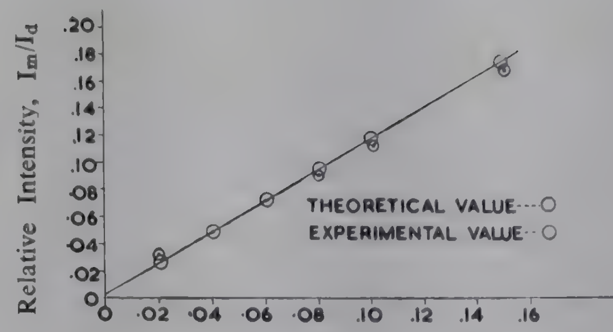

Fig. 1—Comparison of Theoretical Intensity Concentration Curves with Experimental Measurements for Calcite-Dolomite Mixtures

The intensity of the 2.88 Å ($2\theta=30.9°$) dolomite maximum was used as reference line for intensity measurements. Since there were no overlapping lines due to other substances in the desired angular region, the integrated intensity measurements were made directly from the counts. The counts were corrected for the corresponding background value. The observed counting rates were also corrected for the non-linear response of the Geiger counter when the counting rate is high according to Cochran[4] and Klug's[5] methods. All the counts were measured for 64 secs.

Calibration: Jharbeda limestone was used as the base material for calibration because its crystalline character is similar to those of the experimental samples and also appear like that of a pure calcite as observed by minerological investigation[1]. A calibration curve was made with the known mixture of limestone and dolomite (Jharbeda limestone and Rishikesh dolomite; Fig. 2).

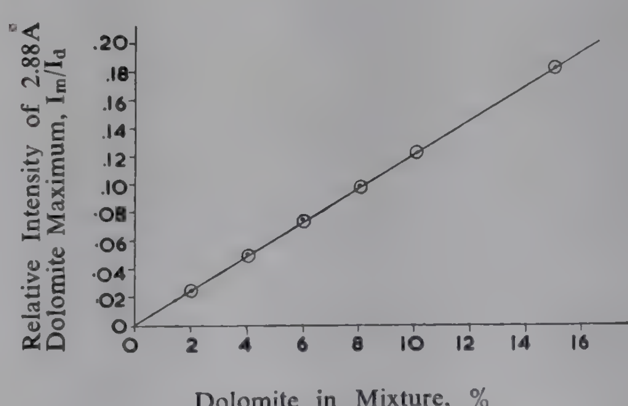

Fig. 2—Working Curve for the Determination of Dolomite in Limestone

Results

The results are shown in Tables 1 and 2. It is seen that although the intensities are corrected for back-

TABLE 1—INTENSITY MEASUREMENTS OF MIXTURES FROM JHARBEDA LIMESTONE AND RISHIKESH DOLOMITE

Dolomite in Mixture, %	*Counts/sec* I_m	I_m/I_d	I_m/I_d *(Theoretical Value vide equation 1)*
2	120	.027	.025
4	220	.050	0.50
6	324	.074	.075
8	420	.097	.099
10	510	.117	.124
15	760	.175	.184

(All values are corrected for background and non-linear response of the Geiger Counter.)

TABLE 2—DOLOMITE CONTENT OF DIFFERENT LIMESTONE SAMPLES

Name of the mineral	*Counts/sec* I_m *(corrected)*	I_m/I_d	*Dolomite as found from the Graph, (Fig. 2), %*
Monda limestone	240	.054	4.4
Dabla limestone	660	.151	12.9
Punjab limestone	380	.086	7.2
Bisra limestone	320	.074	6.1
Purnapani limestone	560	.127	10.8

ground counts, the calibration curve does not pass through the origin (Fig. 2). This extra intensity is caused by the non-x-ray background, due to the cumulative effect of Counter tube and circuit noise, cosmic rays and radioactivity.

The results in Table 2 reveals that the dolomite content of limestone varies with the type of limestone, highest contamination of dolomite being in Dabla sample (13 per cent), while Monda variety is contaminated with the least amount (4.4 per cent). This compares very well with the DTA values.

Precision: The estimated precision of measurement was obtained by replicate values on a given sample (Table 3). The standard deviation of three replicates is 2.8 counts/sec.

Conclusion; The difference between means on different specimen preparation is not statistically significant.

Discussions

For testing whether matrix effect plays a part due to the difference of mass absorption coefficient of calcite and dolomite, a theoretical intensity-concentration curve was drawn following Alexander and Klug's[6] equation. For μ_d not equal to μ_c, the expression for the theoretical analysis curve is given by

$$\frac{I_m}{I_d} = \frac{w_d\ (\mu/\rho)_d}{w_d\,[\,(\mu/\rho)_d - (\mu/\rho)_c\,] + (\mu/\rho)_c} \qquad \ldots.(1)$$

where,

I_d is the intensity of dolomite only,

I_m is the intensity of x-ray diffracted by dolomite, component of the mixture by some selected plane (hkl)

w_d is the weight fraction of dolomite in the matrix,

$(\mu/\rho)_d$ is the mass absorption coefficient of dolomite,

$(\mu/\rho)_c$ is the mass absorption coefficient of calcite.

TABLE 3—VARIATION OF MEASUREMENT BETWEEN SPECIMEN PREPARATIONS

Specimen	*6% Dolomite Intensity, counts/sec.*		
	1	2	3
A	324	326	323
B	327	332	330
C	320	328	321
	Av. 325.66		

ANALYSIS OF VARIANCE

Source	*Sum of the squares*	*Degrees of Freedom*	*Variance*
Within the Column	88	6	14.6
Between the Column	14	2	$3\times7=21$

F, experimental $= \dfrac{S^2_B}{S^2_W} = \dfrac{21}{14.6} = 1.438$

F, critical 95% $\begin{pmatrix} d.f._1 = 2 \\ d.f._2 = 6 \end{pmatrix} = 5.14$

F, experimental $<$ F, critical

The mass absorption coefficient of calcite is 83 and that of dolomite 106. A comparison of the theoretical intensity—concentration curve (Fig. 1), based on calculation from equation (1), with that of the experimental curve (Fig. 2) shows that both are linear, and

the agreement in the relative intensity values is satisfactory. This shows clearly that in spite of the inequality in the absorbing powers of calcite and dolomite, the absorption effect due to the presence of calcite is absent up to the concentration range studies. Hence, direct analysis method can be applied successfully for the estimation of dolomite in calcite.

Acknowledgement

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Kinetics of Dry Box Purification

By

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Iron oxide has been used for more than half a century for the removal of hydrogen sulphide from gas. The design method used for dry boxes however still remains empirical in the sense that an actual trial has to be undertaken on a pilot scale to decide upon the space velocity to be used for a given range of purification. The difficulty is experienced more so when designing an apparatus for low inlet hydrogen sulphide concentration. This paper presents a rational approach to the design based on laws of mass transfer in a fixed bed. Derivation of the basic equation for design is given and a reasonable agreement with experimental and plant data is indicated. The effect of variation of gas velocity on the skip as reported by Hopton is also discussed in relation to the proposed design equation. The presently available methods of design for bulk purification are also reviewed in the light of the proposed new design procedure.

Derivations

Consider a differential element of the oxide bed with a height dH meters through which Q M^3/hr of gas is flowing. The change in the H_2S concentration in passing through this layer will be dC, C being expressed in any convenient unit say mgms of H_2S per M^3 of gas. The mass transfer equation for this zone will then be written as:

$$-Q.\ dC = K_g\ .\ a\ .\ dV.\ (C\text{-}C_o) \qquad \ldots.(1)$$

where 'a' is the mass transfer area offered by one M^3 of the oxide mass and dV is the volume of the oxide mass in M^3 in the differential height dH of the box. C_o is the concentration of H_2S on the oxide side of the stagnant gas interface through which the diffusion occurs, and K_g is the mass transfer coefficient expressed in this case in the nonconventional units, milligrams of H_2S absorbed per unit area per hour per one mgm/nM^3 concentration difference across the interface. If 'A' is the cross sectional area of flow for the oxide box then dV=A × dH. Substituting this value in equation (1) and rearranging

$$-\frac{dC}{C\text{-}C_o} = K_g.\ a\ \frac{A.dH}{Q} \qquad \ldots.(2)$$

It will be seen that $\frac{Q}{A} = v$—the linear gas velocity through the dry box. Therefore

$$-\int_{C_1}^{C_2} \frac{dC}{C\text{-}C_o} = \frac{Kg.\ a.}{v} \int_0^H dH \qquad \ldots.(3)$$

where C_1 and C_2 are the inlet and outlet concentrations of H_2S in gas, and H is the total depth of the oxide bed. The above equation cannot be integrated as it is, unless variation of C_0 with C and the variation K_g with v is known. If we assume that the rate of chemical reaction between iron oxide and hydrogen sulphide is con-between iron oxide and hydrogen sulphide is considerably higher than the rate of diffusion, then the latter will control the overall reaction rate and the value of C_0 will be almost equal to zero or at least negligible in comparison with any value of C. Furthermore, we can assume the value of v to be constant because most of the boxes operate at a linear gas velocity of 7 mm./sec. and this practice has more or less become standard. So also it can be assumed that K_g is not a function of C.

With the above assumptions equation (3) on integration gives:

$$\ln \frac{C_1}{C_2} = \frac{K_g a}{v} \cdot H \qquad \ldots. (4)$$

It will be readily seen that $\frac{v}{H}$ = space velocity. The quantity 'a' is not estimable by any experiment. But one can evaluate the value of $K_g a$, the volumetric mass transfer coefficient from experimental values of C_1, C_2, v and H. If the value of K_g is a function of v then such a relation can be established by conducting the experiment for different values of v.

The soundness of equation (4) can be ascertained by conducting a series of experiments keeping the value of v constant and noting the variation in the value of $\frac{C_1}{C_2}$ with H. A semilog plot in which the quantity H is plotted against $\log_e$ of the ratio $\frac{C_1}{C_2}$ should be straight line whose slope is equal to $K_g a/v$.

Check with Available Data

Extensive data are available both from industrial practice as well as from experiments conducted in this department by the present authors and also by some earlier workers.[1] As a first check, the authors have used the data of Holling and Hutchinson,[2] which are reproduced in most of the standard textbooks[3] on the subject as typical of dry box performance. A semilog plot with these data is shown in the Fig. 1, and the data are reproduced in Table I in metric units. The linear gas velocity used in these boxes has been 25.4 meters/hour. From Fig. 1 it will be seen that all the points fall along a straight line. The value of $K_g a$ calculated from the slope of this line is 73.7.

TABLE 1—Correlation with Holling & Hutchinson's Data on Dry Boxes, Metric Units

(The boxes have a cross sectional area of 0.5 sq.ft/1000 cft. per day of gas. There are four boxes with an oxide depth of 4 ft. in each box. C_1 and C_2 are expressed in mgm/nM^3 of gas and H is expressed in meters.)

C_1	C_2	$\log_{10} \frac{C_1}{C_2}$	H
12590	—	—	0
12590	572	1.3426	1.2192
12590	11.44	3.04154	2.4384
12590	0.2575	4.68920	3.6576
12590	0.03036	5.61768	4.8768

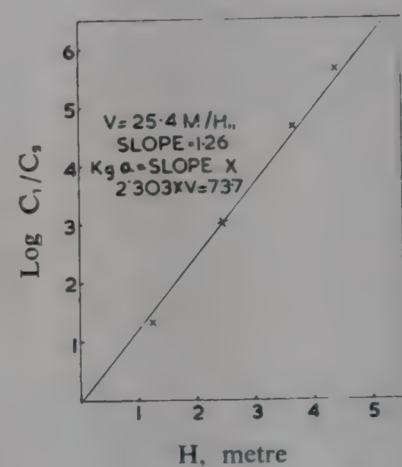

Fig. 1—Correlation with Holling's and Hutchinson's Data

The data obtained by Rao[1] with a pilot unit cannot be correlated in the graphical way as done with the previous data because a fixed bed height H has been used and varying values of C_1 and C_2 for a fixed bed height and fixed linear gas velocity (52.5 m/hr) have been given. For these data the value $K_g a$ can be algebraically calculated using equation (4). selected data from this report and calculated values of $K_g a$ are given in Table 2. It will be seen that the value of $K_g a$ varies from 106 to 115. This is mainly because value of C_1 has not been very steady during these experiments. Secondly the value is higher than that given by Holling and Hutchinson's data.[2] This is explained as due to the oxide mass being different and each oxide mass will have its own value of $K_g a$ for a particular linear gas velocity.

TABLE 2—EXPERIMENTAL DATA ON PILOT PURIFIER BOX

(Tests carried out in a 4″ pipe 4 ft. high space velocity 97.3 v =52.5 M/hr.
H_2S concentrations are given g./100 cubic feet.)

C_1	C_2	$ln\frac{C_1}{C_2}$	Kga=(Space velocity) $\times ln\frac{C_1}{C_2}$
25	8.0	1.1378	110.8
18	6.0	1.0986	106.9
23	7.5	1.1184	108.7
21	6.5	1.1725	114.0
23	8.0	1.0578	102.9
18	5.5	1.1848	115.3
19	6.0	1.1506	112.0
15	5.0	1.0986	106.9

Experimental

The present authors have carried out experiments in a glass tube 2″ dia with a constant linear gas velocity of 7 mm/sec by using 3″, 6″, 9″ and 12″ oxide bed depth. A series of runs were made and of these only those wherein a steady value of bed temperature and inlet H_2S concentration could be maintained are given in Table 3. The data have been graphically correleated in Fig. 2. The value of K_ga as calculated from the slope of this line is 170 which is very much higher because of the highly active, well screened loosely packed oxide used in these experiments. The experiments were conducted at atmospheric pressure and room temperature which was 37°C and did not vary much during the course of experiments.

TABLE 3—EXPERIMENTS IN 2″ GLASS TUBE

(Linear gas velocity 25.2 m/hr. values are plotted in Fig. 2)

C_1 mgm/nM^3	C_2 mgm/nM^3	$log_{10}\frac{C_1}{C_2}$	H meters
427	53.7	0.9	0.305
492	111	0.645	0.229
485	183	0.425	0.152
512	322	0.2	0.076

Discussions

Effect of Linear Gas Velocity: The value of mass transfer coefficient is normally expected to vary directly $(Re)^{0.4}$. Therefore, in given dry box K_ga should vary directly as $(v)^{0.4}$. Hopton[4] has made an interesting

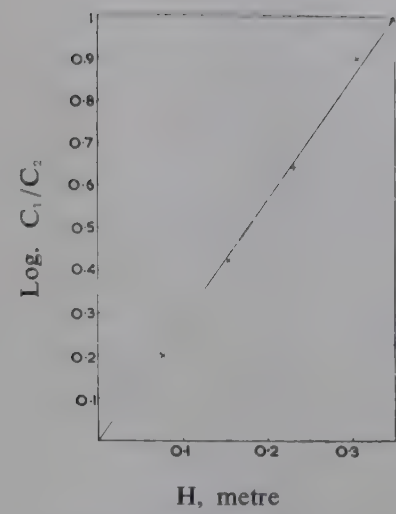

Fig. 2—Experiments in 2″ Glass Tube Linear Gas Velocity 25.2 M/Hr

observation that in laboratory experiments under conditions in which heat losses are relatively high the slip (denoted by symbol S) is independent of H_2S concentration in the gas and that it is increased with increasing gas velocity according to the following equation:

$$\frac{\log S_1}{\log S_2} = \left(\frac{v_2}{v_1}\right)^{0.6} \quad \dots. (5)$$

It will be seen that slip S (which is defined as the fraction of H_2S passing out of the box unabsorbed) is numerically equal to the ratio $\frac{C_2}{C_1}$. Therefore, equation (4) can be rewritten as:

$$\ln\frac{1}{S} = -\ln S = \frac{K_ga}{v}.\ H \quad \dots.(6)$$

In a given dry box therefore for two different linear velocities v_1 and v_2 the following holds true:

$$-\ln S_1 = \frac{(K_ga)_1}{v_1}.\ H \quad \dots. (7)$$

$$\text{and } -\ln S_2 = \frac{(K_ga)_2}{v_2}.\ H \quad \dots. (8)$$

dividing equation (7) by equation (8)

$$\frac{\ln S_1}{\ln S_2} = \frac{(K_ga)_1}{(K_ga)_2}\ \frac{v_2}{v_1} \quad \dots. (9)$$

If we assume according to laws of mass transfer $(K_ga)_1$ as directly proportional to $(v)^{0.4}$ then

$$\frac{(K_ga)_1}{(K_ga)_2} = \left(\frac{v_1}{v_2}\right)^{0.4} \quad \dots. (10)$$

substituting from equation (10) in equation (9)

$$\frac{\ln S_1}{\ln S_2} = \left(\frac{v_2}{v_1}\right)^{0.6}$$ which is the same as equation (5)

given by Hopton. Thus the validity of this newly derived equation as well as the possibility of variation of $K_g a$ with v according to mass transfer laws is also corroborated by Hopton's findings.

In the case of industrial units however the beneficial effect of increased linear velocity is more than offset by increased channelling of gases which reduces the effective area of contact between gas and the active mass and so also by the limited rate of heat dissipation in large units which causes oxide particles to heat up and coalesce at high throughputs. Therefore, for all practical design purposes the variation of $K_g a$ with linear velocity can be neglected for industrial dry boxes.

Application to Design: Use of equation (4) gives the value of critical v/H i.e. space velocity required to attain the necessary purification from inlet H_2S concentration C_1 to the desired outlet concentration C_2. In the design of boxes with bog ore it will be quite safe to assume a value near about 70 for $K_g a$. For any special oxide and special conditions of operation this value must be experimentally obtained.

A box should be designed for a greater quantity of oxide than that indicated by equation (4) because some reserve quantity of the oxide has to be maintained to take into account the inactivation of oxide by prolonged usage. This additional quantity of oxide can be easily ascertained by fixing the duration of the box operation time before it is to be refilled with fresh mass and knowing the H_2S absorption capacity of oxide mass at saturation.

Other Design Formulae: In published literature the following two formulae are available which are recommended for design of boxes.

$$V^1 = \frac{3000\ (D+B)}{f} \qquad \ldots\ (12)$$

$$\text{and } R=1673 \sqrt{c'}\ /\ (F \times W) \qquad \ldots\ (13)$$

Equation (12) has been proposed by Steere Engineering Co., and quoted by "Gas Engineers Hand-book", while equation (13) is commonly used in U.S.S.R.

V^1 = linear gas velocity in ft/hour.
D = depth of the catalyst bed in feet.
B = factor depending on No. of boxes used.
f = factor depending upon inlet H_2S concentration.
R = M^3 of oxide used per 1000 M^3 of gas/hour.
C′ = % sulphur in the gas.
F = % active Fe_2O_3 in a fresh working mass.
W = density of the mass in tons/M^3.

It will be seen that in both of the above formulae the term C_2 outlet H_2S concentration does not appear anywhere. This is because the formulae are intended to be used only for design of boxes to purify gas up to a fixed statutory purity. A designer who desires to design a dry box for fine purification beyond the range of statutory purity will find the above formulae of little use for his purpose. Such a situation arises in considering the purification of carbon dioxide used for urea synthesis. In such a case equation (4) will be more useful.

Nomenclature

Q = M^3/hr. of gas flowing through the oxide mass.
C = Concentration of H_2S in the gas mgms/M^3.
K_g = Mass transfer coefficient. mgms of H_2S transferred per sq. M per hour per (mgm/M^3) concentration difference across the interface.
C_o = H_2S concentration in mgm/M^3 of gas on the surface of the catalyst.
A = cross sectional area of flow for the gas in square meters.
v = linear gas velocity in M/hr. through the oxide mass.
C_1 = inlet H_2S concentration mgm/M^3 of gas.
C_2 = Outlet H_2S concentration mgm/M^3 of gas.
H = depth of the catalyst bed in meters.
a = mass transfer area in square meters offered by one cubic meter of oxide mass.
S = fractional slip of H_2S through the dry box.
P = pressure of operation in atmospheres.
V = linear gas velocity in ft/hour.
D = depth of the catalyst bed in feet.
B = factor in Steere Engineering Formula depending upon the number of boxes.
f = factor in above formulae depending upon inlet H_2S concentration.
R = M^3 of oxide used per 1000 nM^3 of gas per hour.
C′ = % sulphur in gas.
F = % of active Fe_2O_3 in oxide mass.
W = density of oxide mass in tons/M^3.

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Nitrogen Oxides Absorption: Design of Packed Towers

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Design rate and material balance equations have been deduced based on gas phase diffusion of NO_2 and N_2O_4, followed by liquid phase reaction of N_2O_4 with water and verified with available published experimental data. For application of these rate and material balance equations, mass transfer coefficients and equilibrium partial pressures of NO_2 over nitric acid solutions under various conditions have been shown, and the liquid phase reaction velocity constant, the rate constant for reaction of NO with O_2 together with the values of fractional void volume, liquid hold-up and heats of formation have been presented. The design procedure has been specified with an illustration.

Introduction

The design of a nitrogen oxides absorption tower requires data on (a) the rate of absorption of nitrogen peroxides (NO_2 and N_2O_4) in nitric acid solutions of different concentrations; (b) the rate of oxidation of nitric oxide (NO) in presence of free oxygen; (c) the equilibrium relation between NO_2 and N_2O_4; (d) the equilibrium concentrations of nitric oxide (NO) and nitrogen dioxide (NO_2) over nitric acid solutions; (e) the material balance; and the (f) heat balance. While data on (b), (c), (d), (e) and (f) have been well correlated in published literatures, those on absorption of nitrogen peroxides in nitric acid solutions have been correlated by different workers in different ways. To develop a sound design method it is, therefore, pertinent to obtain a good correlation of nitrogen peroxides absorption data.

Chambers and Sherwood[1] tried to correlate their wetted wall tower data on absorption of oxygen-free nitrogen oxides, of more or less a constant composition, in nitric acid solutions of different concentrations based on gas phase diffusion control. Their data at gas Reynold's number of 3000 in a wetted wall tower of 1.46 cm i.d., as plotted by Sherwood and Pigford,[2] shows that mass transfer coefficient $K_{g,\,NO_2}$ is about 0.2lb moles/hr ft^2. atm for dilute acid (less than 40 weight per cent) absorption and the value of K_{g,NO_2} falls rapidly with higher acid concentrations to as low a value as 0.05 lb moles/hr. ft.^{2} *atm.* at 55 weight per cent acid. The value of K_g for NO_2 diffusion through air in a wetted wall tower of 1.46 cm i.d. at gas Reynold's number of 3000 as calculated by the equation given in Sherwood and Pigford[3] is however 0.435 lb moles/hr.ft.^{2} *atm.* This discrepancy was explained by the authors on the basis of appreciable reaction of N_2O_4 with water vapour in the gas phase followed by diffusion of acid mist through the gas liquid interface. Later experiments and analysis by several workers[4–7] in this field show that gas phase reaction and mist formation is not appreciable enough to control the absorption process. Denbigh and Prince[4] unlike Chambers and Sherwood varied the gas composition and acid concentrations and found that the rate of absorption is proportional to concentration of N_2O_4. They, therefore, postulated reaction of N_2O_4 with water in the liquid phase as the controlling step in the absorption process and correlated their data as

$$N_{NO_2}=ka\ \{[N_2O_4] - C\ [N_2O_4]^{\frac{1}{4}}\ [NO]^{\frac{1}{2}}\}$$

where the constant factor C depends on acid concentration. Caudle and Denbigh[5] varied gas composition, acid concentrations as well as gas and liquid velocities and correlated their data as $N_{NO_2}=b\,[N_2O_4]$ for absorption in dilute acids where the constant factor 'b' is a function of gas and liquid Reynold's numbers. They also postulated liquid phase reaction of N_2O_4 as the controlling step and explained the effects of gas and liquid Reynold's numbers as affecting the effective liquid-gas interfacial surface for reaction.

Wendel and Pigford[6] in their experiments in an wetted wall tower on absorption in water of nitrogen oxides of varying composition showed that the rate is controlled by pseudo first order rapid reaction of N_2O_4 with water in the liquid phase as $N_2O_4+H_2O=HNO_3+HNO_2$. They correlated their data as $N_{N_2O_4}=H_{NO_4}\sqrt{k_{N_2O_4}}\ D_{N_2O_4}\ p_{i,N_2O_4}$ so that the rate of absorption in terms of equivalent NO_2 by the overall reaction $3NO_2+H_2O=2HNO_3+NO$, would be $N_{NO_4}=3H_{N_2O_4}\sqrt{k_{NO_4}\ D_{N_2O_4}}\ p_{i,N_2O_4}$. These workers however did not include the effect of back reaction at high acid concentration.

Kramers, Blind and Snoeck[7] in their experiments on absorption of N_2O_4 with water jets showed that

$$N_{N_2O_4}=H_{N_2O_4}\ \sqrt{k_{N_2O_4}D_{N_2O_4}}\left(1+\frac{1}{2k_{N_2O_4}\tau}\right)\ p_{i,N_2O_4}$$

From their experiments and from other published data reported by them the value of $H_{N_2O_4}\sqrt{k_{N_2O_4}\ D_{N_2O_4}}$ was fround to vary between 0.40 —0.81 lb.moles/hr. ft^2. atm. and those of $k_{N_2O_4}$ between 0.9×10^6 to 1.188×10^6 hr^{-1} in the temperature range of 20-40°C. For a contact time (τ) of more than 0.1 seconds, which is usually the condition for industrial practice, the above equation converges to that given by Wendel and Pigford.[6]

Development of A Sound Correlation from Published Absorption Data

Wendel and Pigford's[6] hypothesis of gas phase diffusion of NO_2 and N_2O_4 combined with liquid phase diffusion and reaction of N_2O_4 with water seems to be more plausible. At high acid concentrations the rate of liquid phase diffusion and reaction will be definitely limited by equilibrium partial pressure of N_2O_4 over the acid. So that Wendel and Pigford's[6] equation for a contact time of more than 0.1 second may be modified in the simplified form of $N_{NO_2}=3\ H_{N_2O_4}\ \sqrt{k_{N_2O_4}\ D_{N_2O_4}}\ (p_{i,N_2O_4}\ -p_{eq,N_2O_4})$ (1). Since diffusion coefficient of N_2O_4 is about 0.7 times that of NO_2, the rate of gas phase diffusion of nitrogen oxides in terms of equivalent NO_2 may be expressed as $N_{NO_2}=K_{g,NO_2}\ [(p_{NO_2}-p_{i,NO_2})+1.4\ (p_{N_2O_4}-p_{i,N_2O_4})]$ Assuming continuous equilibrium between NO_2 and N_2O_4, $p_{N_2O_4}$ may be replaced by the equilibrium relationship $p_{N_2O_4}=K_p\ p^2_{NO_2}$ and then equations (1) and (2) may be expressed as $N_{NO_2}=K_{gNO_2}\ [(p_{NO_2}-p_{iNO_2})+1.4\ K_p\ (p^2_{NO_2}-p^2_{i,NO_2})]=3H_{N_2O_4}\ K_p\sqrt{k_{N_2O_4}\ D_{N_2O_4}}\ (p^2_{i,NO_2}-p^2_{eqNO_2})$ (3). Since the contact time in the experiments of Chambers and Sherwood[1] and those of Denbigh and Prince[4] were more than 0.1 second, equation (3) is applicable. Attempts were made to correlate the tabulated data of these authors with a value of $H_{N_2O_4}\sqrt{k_{N_2O_4}\ D_{N_2O_4}}$ in the range of 0.40-0.81 lb moles/hr.ft^2. atm. It was, however, found that the calculated values of K_{g,NO_2} were far higher than those predicted by established equations for gas phase mass transfer coefficients in wetted wall towers. By taking the value of $H_{N_2O_4}\sqrt{k_{N_2O_4}\ D_{N_2O_4}}$ as 1.15 lb moles/hr.ft.^{2} atm. upto 44 per cent by weight acid concentration and 0.445 lb. moles/hr.ft.^{2} atm. between 44 per cent and 60 per cent acid concentration it was found that the calculated value of K_{g,NO_2} agrees fairly with those predicted by already established equations for gas phase mass transfer coefficients in wetted wall towers.

Fig. 1 shows the values of K_{g,NO_2} calculated by

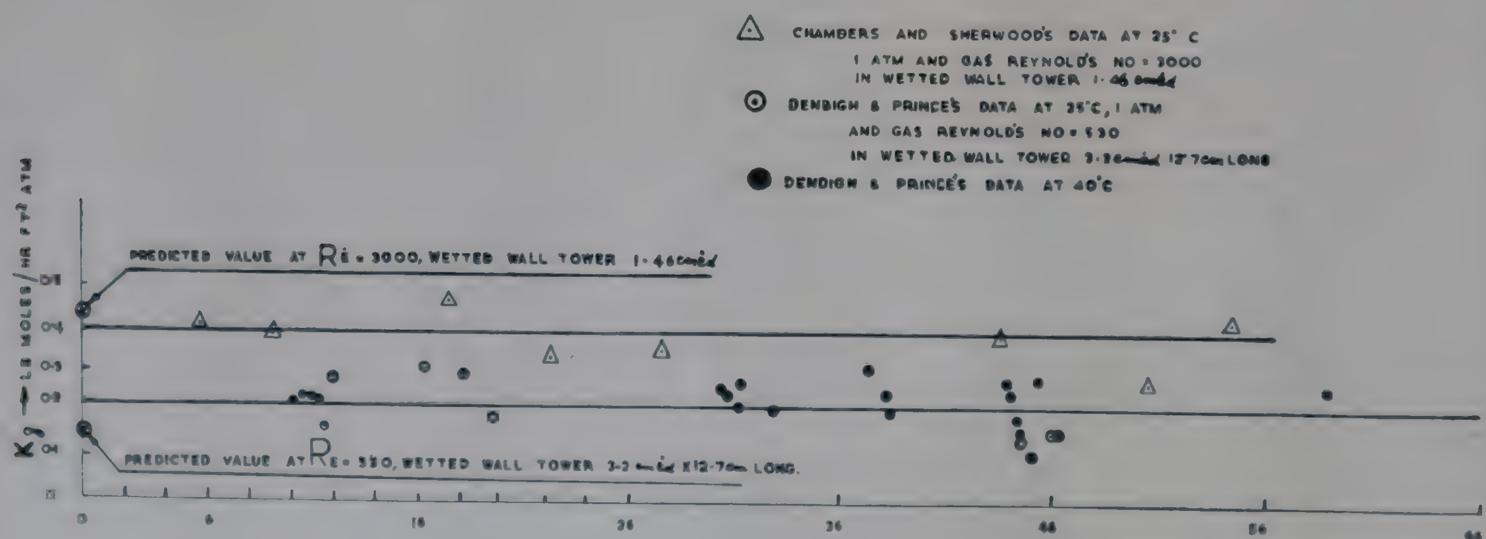

Fig. 1—Kg. Gas Phase Mass Transfer Coefficient for No$_2$, Plotted against Acid Concentration

equation (3) from the representative data on absorption of nitrogen oxides by Chambers and Sherwood[1] at gas Reynold's number of 3000 in a wetted wall tower of 1.46 cm i.d. and from those by Denbigh and Prince[4] at gas Reynold's number of 530 in a wetted wall tower of 3.15 cm i.d. and 12.7 cm long. In these calculations the value of $H_{N_2O_4}\sqrt{k_{N_2O_4} D_{N_2O_4}}$ were taken as 1.15 lb moles/hr.ft². atm. for acid concentration upto 44 per cent and 0.445 lb moles/hr. ft². atm. for acid concentration of 44 to 60 per cent. For comparison the gas phase mass transfer coefficient K_{g,NO_2} at gas Reynold's number of 3000 in a wetted wall tower of 1.46 cm i.d. was calculated by an equation given by Sherwood and Pigford[3] and that at gas Reynold's number of 530 in a wetted wall tower of 3.15 cm i.d. and 12.7 cm long by another equation given by Sherwood and Pigford[8]. The values predicted from these equations are also shown in Fig. 1. These predicted values differ from the actual ones by only 11.5 per cent in the first case and by 27.3 per cent in the second case.

Design Equations for Packed Towers and Equilibrium Relationships

In the absorption of nitrogen oxides in a commercial absorber the following overall reactions take place:

$$3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO \quad \ldots\ (A)$$
$$2NO_2 \rightleftharpoons N_2O_4 \quad \ldots\ (B)$$
$$NO + \tfrac{1}{2}O_2 \rightleftharpoons NO_2 \quad \ldots\ (C)$$

The rate of removal of NO_2 and N_2O_4 by reaction (A) in terms of lb moles of equivalent NO_2 per hour per unit surface has already been given in equation (3). From material balance in the gas phase together with equation (3), the rate of removal of equivalent NO_2 by reaction (A), lb moles per hour, in an elemental volume of packed bed may be expressed as

$$(r_{NO_2})_A = -F\left(\frac{\Delta p_{NO_2} + 2\Delta p_{N_2O_4}}{P}\right)$$
$$= -F\,(\Delta p_{NO_2})_A \frac{(1+4K_p p_{NO_2})}{P}$$
$$= K_{g,NO_2}\, a_e\, S.dl.\ (p_{NO_2} - p_{i,NO_2}) + 1.4\ K_p\ (p^2_{NO_2} - p^2_{i,NO_2}).$$
$$= 3\ H_{N_2O_4} K_p \sqrt{k_{N_2O_4} D_{N_2O_4}}\, a_e\, S.dl.(p_i^2{}_{,NO_2} - p^2_{eqNO_2}) \quad (4).$$

The rate of removal of NO, lb moles per hour, by reaction (C) which is also the rate of creation of NO_2, lb moles/hr by reaction (C) may similarly be expressed as

$$(r_{NO})_c = -F\left(\frac{\Delta p_{NO}}{P}\right)_c = k_c\ p^2_{NO}\ p_{O_2} \Delta\theta \left(\frac{F}{P}\right)$$
$$= -(r_{NO_2})_c = F\,(\Delta p_{NO_2})_c \left(\frac{1+4\ K_p\ p_{NO_2}}{P}\right) \quad (5)$$

Therefore, the effective rate of removal of equivalent NO_2, lb moles/hr, by reactions A and C is

$$(r_{NO_2})_{A+C} = \frac{-F(\Delta p_{NO_2})_{A+C}\ (1+4\ K_p\ p_{NO_2})}{P} \quad (6a)$$
$$= K_{g,\ NO_2}\ a_e\ s.\ dl\ [(p_{NO_2} - p_{i,\ NO_2}) + 1.4\ K_p\ (p^2_{NO_2} - p^2_{i,\ NO_2})] + \left(\frac{F}{P}\right) k_c\ p^2_{NO}.\ p_{O_2}\ (\Delta\theta) \quad (6b)$$
$$= 3H_{N_2O_4}\ K_p\ a_e\ S.\ dl.\ \sqrt{k_{N_2O_4} D_{N_2O_4}}\ (p^2_{i,\ NO_2} - p^2_{eqNO_2}) + \left(\frac{F}{P}\right) k_c\ p^2_{NO}\ p_{O_2}\ (\Delta\theta) \quad (6c)$$

Now the rate of creation of NO by reaction (A), lb moles per hour is equal to one-third the rate of removal, lb moles per hour, of equivalent NO_2 by the same reaction and hence the change in partial pressure of NO by reaction A and C may be expressed as

$$-(\Delta p_{NO})_{A+C} = -(\Delta p_{NO})_c - (\Delta p_{NO})_A$$
$$= -(\Delta p_{NO})_c + \tfrac{1}{3}\ [(\Delta p_{NO_2} + 2\Delta p_{N_2O_4})_{A+C} - (\Delta p_{NO_2} + 2\Delta p_{N_2O_4})_c] \quad (7a)$$
$$= \tfrac{1}{3}\ [(\Delta p_{NO_2})_{A+C}\ (1+4\ K_p\ p_{NO_2})] - \tfrac{2}{3}\ (\Delta p_{NO})_c \quad (7b)$$

From material balance in the gas and liquid phase the rate of acid formation may be expressed as

$$-d(LX) = L_1\ X_1 - L_2\ X_2 \quad (8a)$$
$$= -\frac{F}{P}(\Delta p_{NO} + \Delta p_{NO_2} + 2\Delta p_{N_2O_4})_{A+C} \quad (8b)$$
$$= -\frac{F}{P}[(\Delta p_{NO})_{A+C} + (\Delta p_{NO_2})_{A+C}(1+4\ K_p\ p_{NO_2})] \quad (8c)$$

The equilibrium relationship for reaction (B) is given by Sherwood and Pigford[13] as $K_p = \frac{p_{N_2O_4}}{p^2_{NO_2}}$ where log

$$Kp = \frac{2993}{T} - 9.226,\ atm^{-1} \quad (9)$$

The equilibrium partial pressure of NO_2 over nitric solutions can be calculated from equilibrium constant for reaction (A)

$$K_1 = \frac{p_{eq,\ NO}}{p^3_{eq,\ NO_2}} \quad (10)$$

By material balance equilibrium partial pressure of NO_2 over nitric acid solutions may be related with gas composition as

$$3K_1\ p^3_{eq,NO_2} + 2\ K_p\ p^2_{eq,NO_2} + p_{eq,NO_2} = p_{NO_2} + 2\ K_p\ p^2_{NO_2} + 3\ p_{NO} \quad (11)$$

Application of the Design Equations to A Raschig Ring Packed Tower

The final design rate and material balance expressions and the necessary equilibrium relationships have been shown in equations (6), (7), (8), (9), (10) and (11). For

the application of these equations for a packed tower design, the following data have been shown below:

$a_e\ H_{N_2O_4}\sqrt{k_{N_2O_4}\ D_{N_2O_4}}$

The values of $a_e\ H_{N_2ON_4}\sqrt{k_{N_2O_4}\ D_{N_2O_4}}$. for two commercial sizes of packings have been tabulated in Table 1. The values of a_e have been taken from Yoshida and Koyanagi[9].

TABLE 1

Size of Raschig Ring	*Liquid Rate lbs/hr ft²*.	*a_e ft²/ft³*	*$H_{N_2O_4}\ a_e\sqrt{K_{N_2O_4}\ D_{N_2O_4}}$ lb moles/hr. ft.³ atm* 0–44% acid	44-60% acid
2″	600	8.5	9.80	3.80
	1000	11.0	12.70	4.90
	2000	16.0	18.40	7.10
	4000	20.0	23.00	8.90
1″	600	9.0	10.35	4.00
	1000	13.0	15.00	5.76
	2000	20.0	23.00	8.90
	4000	26.0	29.90	11.50

k_c

The values of the reaction rate constant k_c for reaction (C) has been given by Ermenc[10]. Their values are reported here in Table 2.

TABLE 2—VALUES OF k_c ATM^{-2} SEC^{-1}

Temp. °F	k_c
0	45.0
50	29.7
60	27.2
70	24.7
75	23.8
80	22.7
85	21.8
90	20.9
95	20.0
100	19.3
105	18.6
110	18.0
115	17.4
120	16.8
125	16.2
130	15.6
135	15.0
140	14.5
145	14.0
150	13.5

The calculated values of $K_{g,\ NO_2}a_e\ P$ at 25°C have been shown in Fig. 2 for different gas and liquid rates

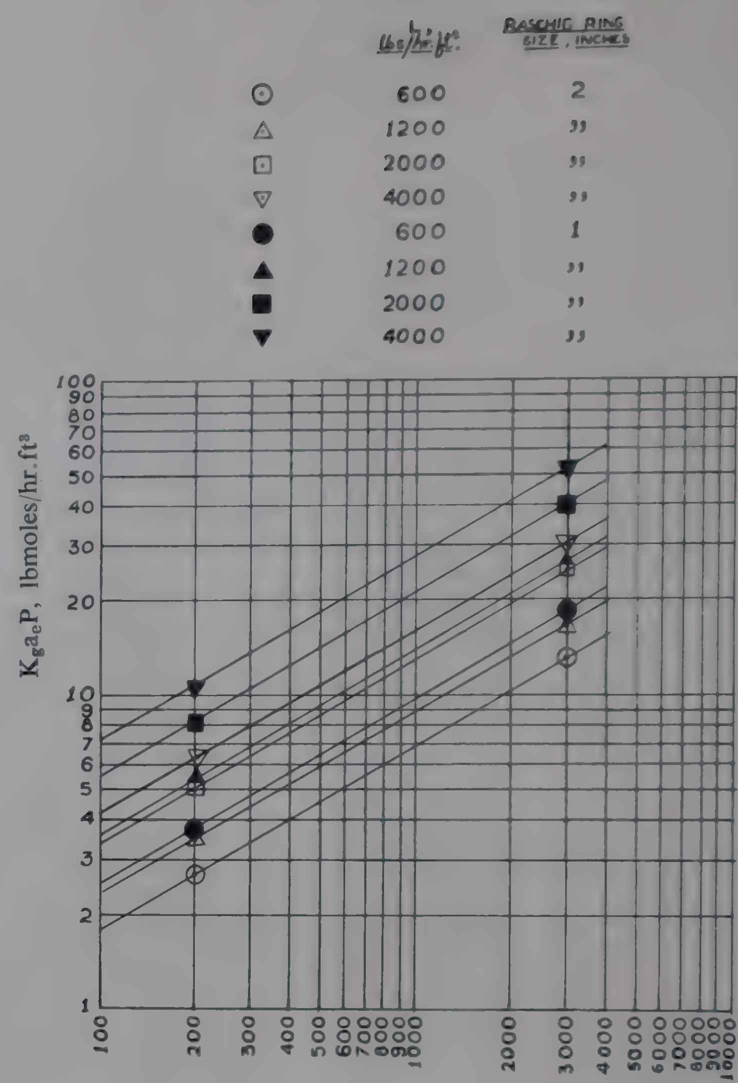

Fig. 2—Value of K_ga_eP for Raschig Ring Packed Towers Against Gas Mass Velocity for Different Liquid Mass Velocities

and for the above two commercial sizes of packings. $K_{gNO_2}a_e$ P will be for all practical purposes independent of pressure and small changes in temperature. Hence from these plots, values of $K_{gNO_2}a_e$ can be calculated at any pressure and temperature involved in nitrogen oxides absorption. For this figure, the K_g values were calculated by the equation.

$$J_D=\left(\frac{K_g,\ p_{BM}}{G_M}\right)\left(\frac{\mu}{\rho D_v}\right)^{2/3}=1.07\left(\frac{G\sqrt{a_p}}{\mu}\right)^{-0.41}$$ given by

Taecker and Hougen[11]. p_{BM} may be taken equal to 0.95P for commercial nitrogen oxides absorption for nitric acid manufacture. Values of $\sqrt{a_p}$ has been given by the above authors as equal to 0.2102 ft for 1″ Raschig and 0.4193 ft for 2″ Raschig ring.

Gas Residence Time θ

The gas residence time θ in a packed tower may be

related with height of packed volume by the following equation,

$$\triangle\theta = \frac{\Delta l}{\left(\frac{G}{\rho}\right) / \{\epsilon\ (1-\psi_1)\}} \tag{12}$$

values of ϵ and ψ_1 may be obtained from Sherwood and Pigford[12, 13]. Their values are reported in Table 3.

TABLE 3—VALUES OF FRACTIONAL VOID VOLUME & LIQUID HOLD-UP

Size of Raschig Ring	*Liquid Rate lbs/hr ft²*	*Void Volume Fraction of packed Vol.*	*Liquid hold-up fraction of void volume*
1″	600		0.017
	1000	0.68	0.024
	2000		0.038
	4000		0.060
2″	—	0.83	—

Equilibrium Partial Pressure of NO_2 over Nitric Acid Solutions

Figs. 3, 4 and 5 show the equilibrium partial pressure of NO_2 over nitric acid solutions at 35°C, 40°C and 45°C against acid concentration for various gas composition. These figures have been drawn based on equation (12) using values of K_1 and K_p from Sherwood and Pigford[14].

From these data, the design rate and material balance equations can be easily solved for an elemental volume of bed giving changes in partial pressures of NO, NO_2 and N_2O_4 and the changes in concentration of nitric acid solutions obtained in this small volume. Knowing this the heat generation in this small volume can be calculated from the data on heats of formation given by Rossini and Bichowsky[15]. These values are being reproduced in Table 4.

Illustration

Nitrous gas of the following composition enters the absorption system. To evaluate the change in gas composition as it passes through tthe oxidation tower and the first stage of NO 1 absorption tower.

Composition of the gas

Components	*Normal cuft/hr.*	*Percent by volume*
NO	73,200	6.75
NO_2	8,050	0.74
O_2	94,500	8.72
Rest	907,300	83.70

Inlet Temperature = 50°C
Pressure = 4 ata.

TABLE 4—HEATS OF FORMATION AT 18°C

Substance		*Heat of formation cal/gm mol.*
H_2O (liquid)		−68,315
NO (gas)		21,600
NO_2 (gas)		8,030
N_2O_4 (gas)		3,060
HNO_3 (liquid)		−41,660
Do (∝dilution)		−49,190
,, 6400	moles water/mol HNO_3	−49,154
,, 3200	,,	−49,142
,, 1600	,,	−49,129
,, 800	,,	−49,116
,, 400	,,	−49,105
,, 200	,,	−49,100
,, 100	,,	−49,104
,, 50	,,	−49,124
,, 25	,,	−49,162
,, 20	,,	−49,120
,, 10	,,	−48,980
,, 5	,,	−48,330
,, 2	,,	−46,440
,, 1	,,	−44,950

In the oxidation tower 93 t./hr of 53% acid is circulated to maintain gas at an average temperature of 45°C. This acid also prevents absorption of NO_2 in water.

In the first stage of NO I absorption tower 93 t./hr of 53% acid is also circulated to prevent excessive rise in temperature and also to maintain proper L/G ratio. The gas temperature is maintained at an average value of 40°C. The average temperatures of the liquid are maintained at 45°C in the lower half and at 40°C in the upper half of this absorption stage. The product from the bottom of this stage is 32,500 lbs/hr acid of 53% strength.

The following dimensions of the towers and packings are recommended:—

Oxidation tower

Diameter	=8′ 10½″
Height	=66′ 8½″
Packed volume	=2588 ft.³
Size of Packings (Raschig rings)	=2″

First stage of NO I absorption tower:

Diameter	= 8′ 10½″
Packed height	=10′ 6″
Size of Packings (Raschig rings)	=2″

Solution

Calculation of Fraction NO Oxidized in the Oxidation Tower: From Table 3, $\epsilon = 0.83$, $\psi_1 = 0.06$ and the free space beyond packings is about 37% of tower

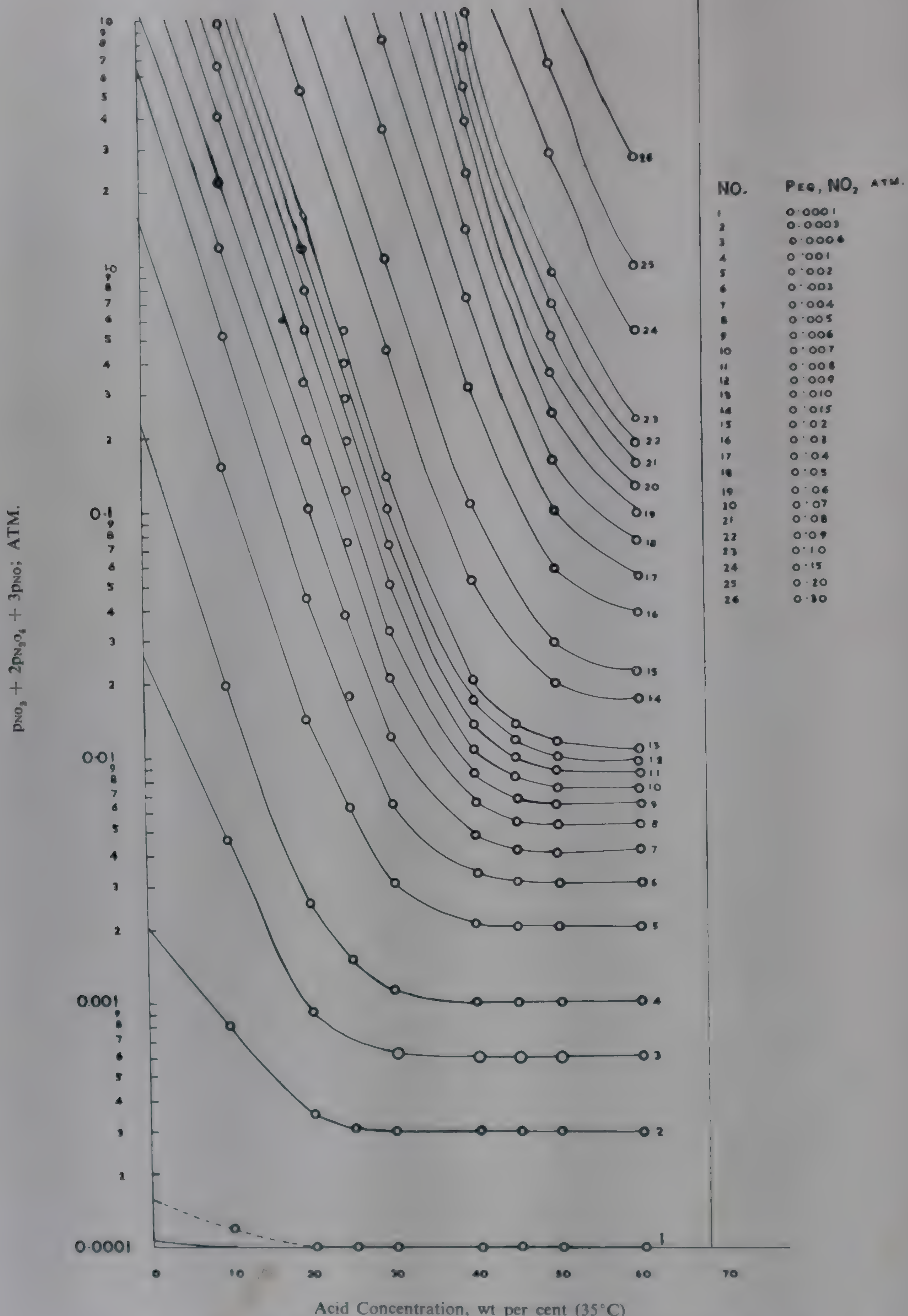

Fig. 3—Equilibrium Partial Pressure of NO_2—Effects of Gas Composition and Acid Concentration

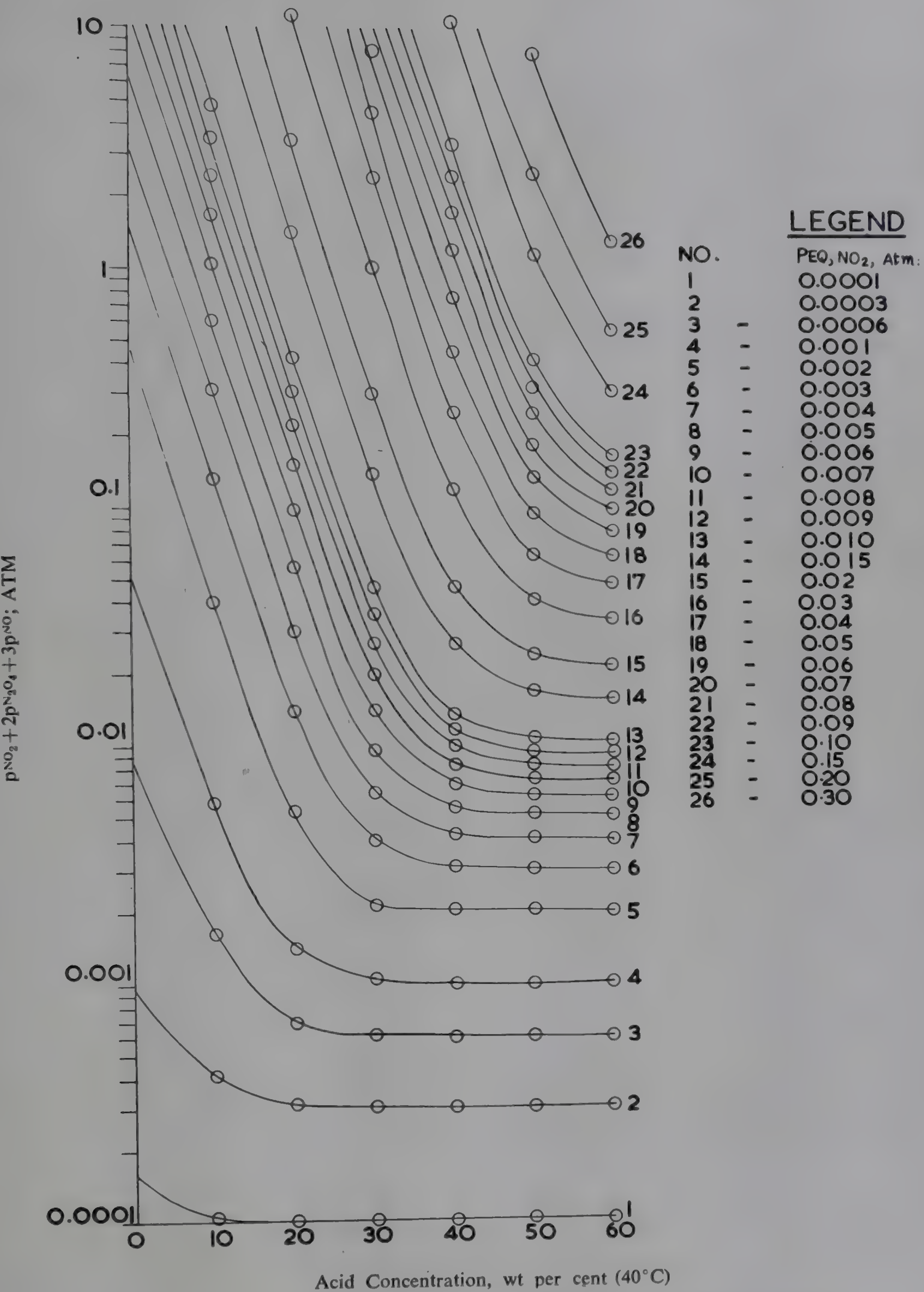

Fig. 4—Equilibrium Partial Pressure of NO_2—Effects of Gas Composition and Acid Concentration.

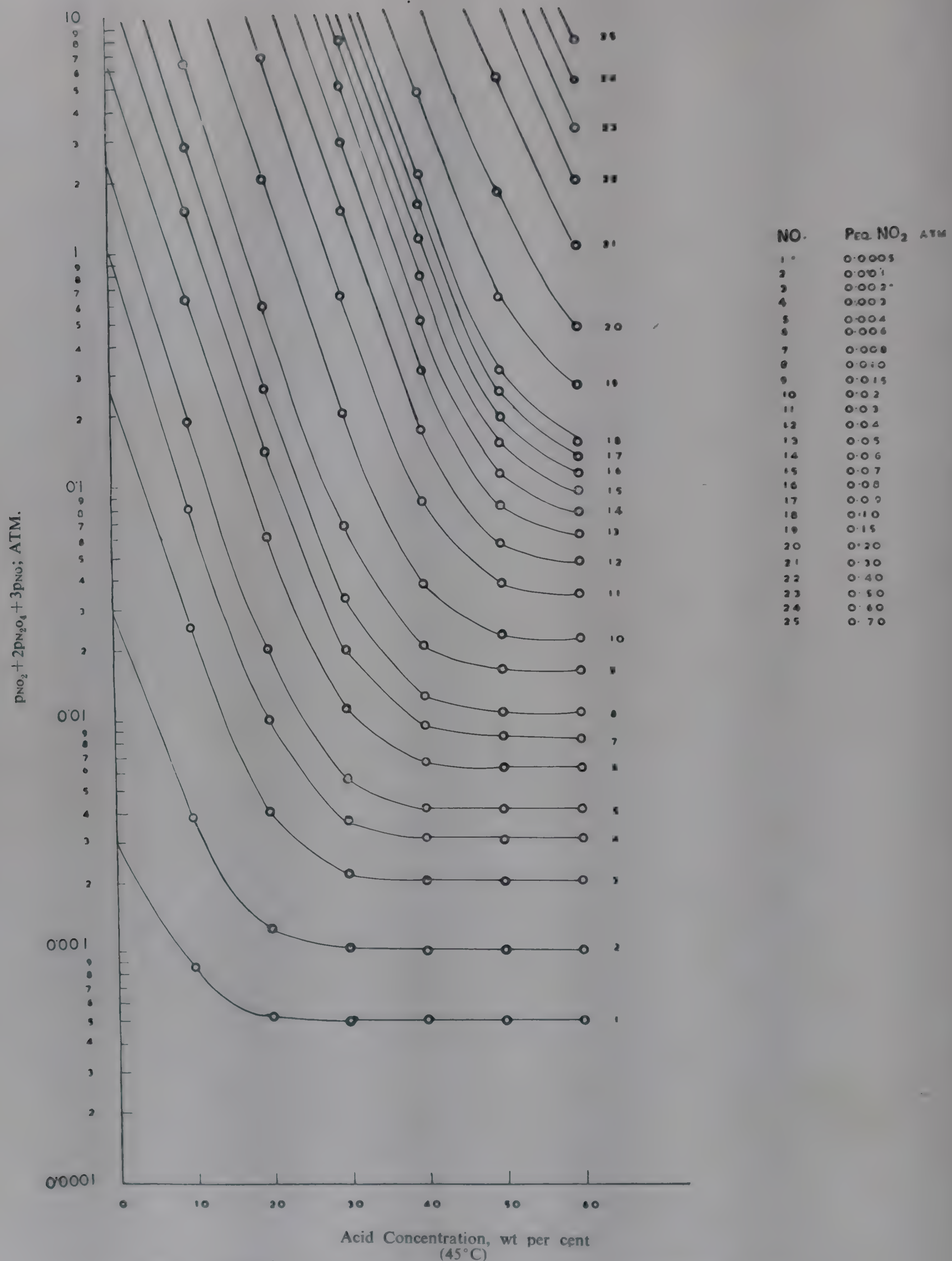

Fig. 5—Equilibrium Partial Pressure of NO_2—Effects of Gas Composition and Acid Concentration.

volume. Hence from equation (12) residence time $\theta = 40.3$ seconds. Equation (5) may be written as $(-\Delta p_{NO})_c = k_c\ p^2_{NO}\ p_{O_2}\ (\Delta\theta)$. An approximate integrated from of this equation may be expressed as

$$\frac{1}{(p_{NO})_2} = \frac{1}{(p_{NO})_1} + 2\,[(p_{O_2})_1 - (p_{NO})_1]\ k_c\ \theta/2.$$

where subscripts 1&2 refer to initial and final conditions. At gas temperature 45°C, $k_c = 17.2$ atm^{-2} sec^{-1}. Hence $(p_{NO})_2 = 0.0064$. Fraction oxidised is about 93%. Hence the gas composition after oxidation is

Components	*Normal cuft/hr*	*% by volume*
NO	1,680	0.1600
NO_2	45,000	4.3125
$2N_2O_4$	34,400	3.2950
O_2	58,500	5.6100
Rest	907,300	86.8000

Evaluation of Gas Composition at the Outlet from the First Stage of NO I Absorption Tower: The first stage of NO I absorber is divided into two sections having 5.25 feet packed height each, the average gas temperature in each section is assumed 40°C and the average liquid temperatures are assumed 45°C in the lower section and 40°C in the upper section. Pressure in the system is 4 ata. From equation (9), value of K_p at 40°C gas temperature $= 2.21$ atm^{-1} and from Table 2 value of k_c at 40°C gas temperature is equal to 18.6 atm^{-2} sec^{-1}. The acid circulation rate is 3,500 lbs/hr ft², and the gas mass velocity, G is equal to 1,440 lbs/hr. ft².

Hence, from Table 3 values of ϵ & ψ_1 for 2″ Raschig ring packed tower are 0.83 and 0.06 respectively and from Table 1 the values of $H_{N_2O_4}\ a_e\ \sqrt{k_{N_2O_4}\ D_{N_2O_4}}$ for 2″ Raschig ring packed tower are 21.9 and 8.5 lb moles/hr. ft³. atm for 0-44% and 44-60% acid respectively. From Fig. 2 the value of $K_g\ a_e\ P$ is equal to 19 lb moles/hr ft³. Hence $K_g\ a_e$ is equal to 4.75 lbs moles/hr ft.³ atm. (P=4 ata).

From the given gas flow rate, F=2,910 lb moles per hour. The packed volume for each section is equal to 324 ft³. Acid production rate from the bottom of this absorption stage is equal to 1,121 lbs moles/hr of 53% acid (0.245 molefraction HNO_3).

From the above data the residence time is each section is equal to 2.9 seconds (calculated from equation 12).

With this information the gas compostion at the outlet of each section and the rate of acid formation may be calculated. For this calculation the following procedure is suggested.

The inlet partial pressures of nitrogen oxides and their combinations together with that of Oxygen are tabulated (Table 5). A value of p_{NO_2} at the outlet from any packed section is assumed. From this assumed value, $p_{N_2O_4}$ is calculated by equilibrium relationship (equation 9). By trial and error p_{NO} at the outlet is determined from equation (7) in the following way. Assuming an average value of p_{NO} in the bed $(\Delta p_{NO})_c$ is calculated from equation (5). Putting this value of $\Delta(p_{NO})_c$ in equation (7), $(\Delta p_{NO})_{A+C}$ and hence the average value of p_{NO} is determined and then checked with the assumed one.

The value of $p_{eq,\ NO_2}$ is now calculated from Figs. 3, 4 and 5. Since the acid circulation rate is about 7 times the acid production rate, the acid strength in both the sections of this absorption stage may be assumed constant at 53 per cent.

From equations (6b) and (6c) $p_{i,\ NO_2}$ is calculated. With this value of $p_{i,\ NO_2}$ the values of $(\Delta p_{NO_2})_{A+C}$

TABLE 5—Inlet & Outlet Partial Pressures of Nitrogen Oxides & Their Combinations

Partial pressure, atm.

Components	*Lower section*			*Upper section*		
	Inlet	*Outlet*	*Average*	*Inlet*	*Outlet*	*Average*
NO	0.0064	0.0262	0.0174	0.0262	0.0394	0.0327
NO_2	0.1725	0.1455	0.1575	0.1455	0.1160	0.13075
N_2O_4	0.0659	0.0467	0.0555	0.0467	0.0297	0.0372
$NO_2+2N_2O_4$	0.3043	0.2389	—	0.2389	0.1754	—
$NO+NO_2+2N_2O_4$ ..	0.3107	0.2651	—	0.2651	0.2148	—
$3NO+NO_2+2N_2O_4$ ..	0.3235	0.3175	0.3205	0.3175	0.2934	0.3055
O_2	0.2244	0.2229	0.2236	0.2229	0.2174	0.2202

and p_{NO_2} at outlet are calculated from equations (6a) and (6b). This value of p_{NO_2} at the outlet is then checked with the assumed value. The rate of acid formation is now calculated from equation (8b). Total acid formed in this absorption stage is 73.3 lb moles/hr. Hence the inlet acid concentration to this stage is calculated from equation (8a) as 0.1850 molefraction i.e. 44.3 per cent by weight. In this absorption stage it may be now easily found that the components participating in reactions (A) and (C) are either destroyed or created by the above reactions at the following rates.

Components	*Rate of Destruction or Creation, lb moles/hr.*
NO	+23.35
NO_2	−43.20
N_2O_4	−26.70
HNO_3	+73.30
H_2O	−34.85

Hence from the heats of formation data given in Table 4 the amount of heat liberated is equal to 1.61×10^6 Btu/hr. The specific heat of 53% HNO_3 at 40-45°C is 0.68. Hence the liquid temperature will rise by about 6.3°C.

Nomenclature

a_e =effective gas-liquid interfacial surface ft² per ft³ packed volume.

a_p =external and internal surface of a single piece of packing, ft².

b =constant, depends on gas and liquid Reynold's number.

c =constant, depends on acid concentration.

$D_{N_2O_4}$ =diffusion coefficient of N_2O_4 in the liquid phase, ft²/hr.

D =diffusivity of any component through gas phase ft²/hr.

F =gas flow, lb moles/hr.

G =gas flow, lbs/hr ft². of total cross section.

G_M =gas flow, lb moles/hr ft². of total cross section.

$H_{N_2O_4}$ =Henry's law constant for solution of N_2O_4 in nitric acid solution lb moles/(cuft) (atm).

k_a =rate coefficient, ft/hr.

$k_{N_2O_4}$ =rate constant for reaction of N_2O_4 with water in the liquid phase, 1/hr.

k_c =rate constant for reaction of NO with O_2. atm^{-2} Sec^{-1}.

K_1 =equilibrium constant for reaction (A) atm^{-2}.

K_p =equilibrium constant for reaction (B) atm^{-1}.

K_g =gas phase mass transfer coefficient for any component, lb moles/hr ft². atm.

K_{g, NO_2} =gas phase mass transfer coefficient for NO_2 lb moles./hr. ft². atm.

L =liquid flow, lb moles/hr.

L_1 = ,, ,, at the gas entrance

L_2 = ,, ,, at the gas exit

l =height of packed volume ft.

N_{NO_2} =rate of absorption of nitrogen oxides in terms of equivalent NO_2, lb moles/hr ft².

$N_{N_2O_4}$ =rate of absorption of N_2O_4, lb moles/hr ft².

$[N_2O_4]$ =concentration of N_2O_4, lb moles per cuft.

p_{eq, NO_2} =equilibrium partial pressure of NO_2 over nitric acid solutions, atm.

p_{i, NO_2} =partial pressure of NO_2 at the gas-liquid interface, atm.

p_{eq, N_2O_4} =equilibrium partial pressure of N_2O_4, over nitric acid solution, atm.

$p_{iN_2O_4}$ =partial pressure of N_2O_4 at the gas-liquid interface, atm.

p_{NO_2} =partial pressure of NO_2, atm.

p_{NO} =partial pressure of NO, atm.

$p_{N_2O_4}$ =partial pressure of N_2O_4, atm.

p_{BM} =mean partial pressure of inerts, atm.

P =total pressure, atm.

$(r_{NO_2})_A$ =rate of removal of NO_2 and N_2O_4 by reaction (A) in terms of lb moles of equivalent NO_2 per hour.

$(r_{NO_2})_{A+C}$ =rate of removal of NO_2 and N_2O_4 by reactions (A) and (C), lb moles of equivalent NO_2 per hour.

$-(r_{NO})_A$ =rate of production of NO by reaction (A), lb moles/hr.

$(r_{NO})_{A+C}$ =rate of removal of NO by reaction (A) and (C), lb moles/hr.

$-(r_{NO_2})_C$ =rate of production of equivalent NO_2 by reaction (C)., lb moles/hr.

$(r_{NO})_C$ =rate of removal of NO by reaction (C), lb moles/hr.

S =tower cross section, ft².

T =absolute temperature, degrees Kelvin

X =molefraction HNO_3 in the liquid phase.

Greek letters

θ=gas residence time, hours.
ρ=gas density, lbs per cu.ft.
ϵ=fractional void volume, cu. ft per cu. ft packed volume.
ψ_1=liquid hold-up as fraction of void volume, cu.ft per cu.ft.
μ=viscosity of gas, lb/(ft) (hr).

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Ureolytic Bacteria in Soil
I—A Technique for their Detection

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A method for the detection of ureolytic bacteria in soil is described. 5ml. of the sterile liquid media containing urea and phenol red indicator was inoculated with about 0.5g. of freshly but aseptically collected soil and incubated in the laboratory. During hydrolysis of urea, ammonia is released and the colour of the liquid media changes from yellow to red. The process is very slow during the first 24 hr. but quite rapid later, and is almost complete in about 72-96 hr. Evidences have been presented that the hydrolysis is effected by bacteria developing from soil during incubation.

In the case of very alkaline soil, the procedure may be modified by using small pieces of organic matter from soil as inoculum after washing thoroughly in sterile water. Ureolytic bacteria have been shown to be associated with these. This eliminates any chances of soil *urease*, if already present, from being carried into the culture tube in substantial quantity and supports effectively the bacterial hydrolysis of urea.

Introduction

The hydrolysis of urea in soils is an important factor governing its application as fertilizer. This transformation is no doubt dependent on many factors, of which the role of soil microorganisms endowed with ureolytic activities is the prominent one. The distribution of these organisms in different soil types is likely to follow a pattern according to their growth requirements.

Though a knowledge of this ecological aspect of soil microorganisms is much desired, yet very little information is available at present. A study into the problem of urea hydrolysis by soil microorganisms was, therefore, taken up.

In view of the urgency of supplying nitrogenous fertilizers for crop production, a quick assessment of different soils for their urea-hydrolysing potentiality is badly needed. An attempt was, therefore, made to develop a technique for this purpose. The method, described here, is based on the development of alkaline reaction in the liquid medium due to the liberation of ammonia above a certain concentration from urea during hydrolysis[1]. This change of pH is easily detectable by using a suitable indicator in the medium.

Experimental

Soil samples (25 random samples from each plot) were collected in sterilized *petri* dishes separately from the newly-developed plots in the farm of this division, and about 0.5 g. of a well-mixed sample was then added to 5 ml. sterilized liquid medium** in test tubes, and incubated at room temperature (28-32°C) with a known amount of NH_3-free urea (resulting concentration of nitrogen in the medium varying from 500 to 800 ppm) in the laboratory. During hydrolysis, ammonia is released, and when the concentration of ammonia reaches about 239 ppm—discussed in the later part of this paper—the resultant alkaline reaction is indicated in the medium** by the change of colour of the phenol red indicator from yellow to red. The control was maintained in order to check the possible sources of errors due to (1) the release of ammonia from the decomposition of proteinaceous organic matter present and (2) the alkaline pH of the soil used. The estimation of ammoniacal nitrogen was done by Nessler's reagent colorimetrically.

Results and Discussions

The result of one of the representative experiments, conducted so far, is given in Table 1.

TABLE 1—Hydrolysis of Urea in Liquid Media Inoculated by Soil

Name of Plots with Crops Growing at the Time of Sample Collection	*Percentage of Tubes Showing Red Colour* — *Media+Urea No Soil Added Control A*			*Media+Soil No Urea Added Control B*			*Media+Soil +Urea*		
	Incubation Time, hr.								
	24	48	72	24	48	72	24	48	72
Plot AL_4 (Brinjal)	0	0	0	0	0	0	0	90	100
,, AU_4 (Sugarcane)	0	0	0	0	0	0	0	85	100
,, BU_1 (Potato)	0	0	0	0	0	0	0	75	100
,, BU_3 (Boro Paddy)	0	0	0	0	0	0	0	70	100

It may be noted that during the first 24 hr. of incubation, no change of colour was obtained but the medium became quite turbid due to bacterial growth and pH went down to 5.1. Observations taken after 48 hr, however, indicate a good progress with the hydrolysis as in 70-90 per cent of the tubes containing urea and inoculated with soil, red colour developed during this period. Incubation for 72 hr. have resulted in the development of red colour in all these tubes indicating that ammonia nitrogen has been released above 250 ppm. in all the tubes during this period (Table 3). The controls, however, did not show any such colour even after 5 days. This indicates that the probable sources of error anticipated above have not vitiated the results.

The evidence of urea hydrolysis was further substantiated by direct estimation of ammoniacal nitrogen, in separate experiments run simultaneously using 500 ppm. as urea-nitrogen initially. It may be seen from Table 2 that

TABLE 2—Hydrolysis of Urea by Soil Microorganisms

Nature of Inoculum	*Ammoniacal Nitrogen, ppm* — *Period of Incubation, hr* 24	48	72	96
Soil	12.7	389.0	460.0	500.0
Washed organic matter	34.0	415.0	462.0	500.0

TABLE 3—Changes of pH with the Concentration of Ammoniacal -N in the Liquid Media Inoculated and Incubated for 24 hr.

pH	*Ammoniacal Nitrogen, ppm*	*Colour of Media*
5.1	0	Yellow
6.6	119.6	,,
7.4	199.2	,,
7.6	218.9	,,
7.8	238.8	Red colour just appears
8.0	249.2	Red colour distinct

** Composition of liquid medium: Peptone 1 g.; KH_2PO_4, 2 g.; NaCl 5 g.; Sucrose 1 g.; Phenol red indicator, (0.2% alc. solution), 10 ml. and Dist. Water 1000 ml., pH adjusted to 6.8.

the amount of NH_3-nitrogen released from urea after 24 hr. is hardly appreciable (12.7 and 34.0 ppm), while the estimations done after 48,72 and 96 hr. reveal that the concentrations of the same during these periods are considerably high, and the addition of phenol red turns the colour of the liquid into intense red.

It is true that the catalytic decomposition of urea in soil[2-7] may take place due to the presence of an enzyme, viz. *urease*[8], but the amount of soil (0.5 g.) used is less likely to carry sufficient amount of *urease* required for urea hydrolysis in tubes. It has also been noted that if *urease* is supplied in the culture medium containing urea, sufficient hydrolysis takes place to develop intense red colour within 1/2 hr. or so at room temperature (28-32°C). But this was never the case when soil was used. Had there been any appreciable amount of *urease* present in soil at the time of its collection, the incubation period for the development of red colour would have been much less. Alternatively, a sufficient amount of *urease* has been elaborated in the medium as a result of the growth of bacteria for 24 hr., and hence any indication of urea hydrolysis is obtained only after this period of incubation.

This concept of bacterial participation in urea hydrolysis was further substantiated by the following observations. (A) Sterilized liquid media with indicator were inoculated by 2-3 small pieces of organic matter (length 4-6 mm.) picked up from soil and washed several times in sterile water[9] in order to remove contaminated urease, if any. After incubation for 24 hr., the liquid became quite turbid due to appreciable amount of bacterial growth. Urea was then added. The media became red within 4-5 hr., indicating hydrolysis of urea.

(B) In another series of experiments, 5 ml. of sterilized media in tubes was inoculated separately by (1) 0.5 g. soil, (2) 2-3 pieces of washed organic matter and (3) mixed culture of bacterial suspensions taken from the tubes incubated for 24 hr. after inoculation by soil or washed organic matter. These were then incubated after adding streptopenicillin (1 mg./5 ml. media), in some of the tubes, in order to prevent bacterial growth. Urea was added after 24 hr. It was noted that hydrolysis could take place only in tubes in which bacterial growth was appreciable but not in those where growth was prevented by antibiotics. But if *urease* is added in tubes with no bacterial growth due to the presence of streptopenicillin, hydrolysis proceeds as usual.

It thus seems clear that the hydrolysis noted in the present experiments with the farm soil has been effected by the bacterial *urease* developed as a result of bacterial growth and no evidence of its presence in sufficient quantity in the soil used seems to be forthcoming. The results also indicate that the ureolytic organisms present in the farm soils are more or less uniformly distributed throughout the plots.

Conclusions

A technique for the detection of ureolytic bacteria in cultivated soil has been presented. 5 ml. of sterile liquid medium in tubes containing urea and phenol red as indicator is inoculated by about 0.5 g. of freshly but aseptically collected soil and incubated for 3-4 days at room temperature (28-32°C). Pieces of organic matter picked up from soil and thoroughly washed in sterile water or mixed bacterial suspensions developed into the media after inoculation by soil or organic matter, may also be used. The ureolytic bacteria, if present, will grow out of the inoculum (soil or organic matter) and the hydrolysis of urea will follow.

The yellowish liquid medium in the tube becomes strongly alkaline due to the accumulation of free ammonia and turns red. The organisms may then be isolated in pure culture and identified.

The following two factors may probably interfere and may lead to wrong conclusions: (1) The release of ammonia from proteinaceous organic matter present in soil and (2) the soil reaction. As regards the first factor, the following observations were made. The pH of liquid after incubation for 24 hr. with soil or organic matter was correlated with the concentrations of amoniacal nitrogen by adding NH_4OH solution of known strength. It is seen from Table 3 that the minimum concentration of ammoniacal nitrogen in the medium should be about 238.8 ppm in order to change the pH from 5.1 to 7.8 when the pink colour just appears. If the concentration is 249.2 ppm. the pH is 8.0, and the red colour becomes quite distinct. The use of 0.5 g. soil as has been suggested for the present technique may, no doubt, release some ammonia from soil organic matter but in order to get a concentration of as high as 238.8 ppm. of ammoniacal nitrogen in 5 ml. liquid medium used, this amount of soil must yield 1.194 mg. ammonium-nitrogen which is most unlikely, especially during such a short period of incubation (3-4 days).

Secondly, it was considered whether alkaline soil might interfere by raising the pH of the test medium. But actual experience with alkaline soil (the pH of the farm soil used in the present experiments varied from 7.5 to 8.0) did not show any such interference. It is also quite improbable for an alkaline soil to render

alkalinity equivalent to or more than 239 ppm. of ammoniacal nitrogen, which is necessary to develop the desired pH to show the colour change of the test medium.

If, however, some difficulty is experienced with some soils, the procedure may be modified by using washed organic matter or mixed bacterial suspensions from liquid media inoculated by soil or organic matter.

It seems probable that this method may be used as a standard technique for detection of ureolytic bacteria in different soil types under various agro-climatic regions in India but definite conclusions can be drawn only after intensive verification.

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Mineralization of a Urea-Formaldehyde Compound in Some Indian Soils

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Mineralization of a urea-form compound has been studied under laboratory condition in some Indian soils, and the same has been compared with that of urea. The experiments indicated that the urea-form compound mineralized slowly but progressively throughout the incubation period in all soils except in the Netarhat acid clay, while urea decomposed almost completely within the first few weeks. Mineralization of the urea-form compound appeared to depend upon the initial soil pH, the value increasing with decreasing pH. The highest mineralization was observed in the soil with initial pH of 5.90, both in the cases of urea-form and urea. Appreciable quantities of ammonium-nitrogen persisted in acidic soils even after 14 weeks' incubation, while these decreased to low levels in alkaline soils. Nitrate-nitrogen recovery was higher in alkaline soils than in acid or neutral soils in both the treatments.

Introduction

Urea-formaldehyde fertilizers popularly known as 'urea-form', have certain advantages over the other nitrogenous fertilizers of present day use, such as urea, ammonium sulphate, etc. The major advantages are due to their low solubilities by virtue of which they release their nitrogen slowly, but uniformly, to plants throughout their growing periods, and are far less subject to loss by leaching. The suitability of such materials for use as a source of controlled nitrogen availability to long term crops particularly turf and other grasses, home garden, green-house and ornamental plants have been well established.

It is generally known that the growing plants take up nitrogen mostly either in the form of ammonium or nitrate or both. In order to evaluate a fertilizer, therefore, it becomes essential to study its mineralization in soils under various conditions. Vegetative and

laboratory studies[1, 2, 6–16] indicate that the mineralization of a urea-form material depends primarily upon the mole ratio of its constituents and method of preparation. Mineralization is also said to depend upon such soil properties as texture, structure, pH, buffer capacity, microbiological activities, nutrient status and climatic conditions including temperature and moisture.[4, 8, 14]

Since not much work appears to have been done on Indian soils with this fertilizer material, it was thought useful to undertake the present study to have some idea about the mode of mineralization of one such compound in a few soils of this country, particularly in relation to pH, and as compared to urea.

Experimental

Five soils ranging in pH from 5.25 to 8.30 were used (Table 1). These were air-dried and ground to pass a 2 mm. sieve. 200 g. of each was taken in one litre beaker to which was added the powdered (less than 20 mesh B.S.S.) urea-formaldehyde compound at the rate of 25 mg. of nitrogen per 100 g. of soil on oven dry basis. The urea-form material was mixed thoroughly with the soil, and distilled water was added to 50 per cent of its moisture-holding capacity. The moist soils were then incubated at room temperature and the loss of moisture was replenished occasionally. After 1, 2, 4, 6, 10 and 14 weeks of incubation, samples were taken out for ammonium and nitrate-nitrogen determinations. The pH of the samples at the end of the experiment was determined using a glass-calomel electrode Cambridge pH-meter, at 1:2.5 soil (air-dry): water ratio. The pH of the Netarhat* clay soil was determined also at the end of 10th week incubation period. Ammonium-nitrogen was determined by leaching the soil with 6 per cent sodium chloride solution (previously adjusted to pH 2.5 with dilute hydrochloric acid), distilling the leachate with magnesia, absorbing the liberated ammonia in hydrochloric acid, and back-titrating with a standard alkali. Nitrate-nitrogen was determined colorimetrically by nitro-phenol-disulphonic acid yellow colour method[3] using a photoelectric colorimeter.

A similar experiment was started simultaneously with urea as a source of nitrogen for comparison. A control sample was also included in each series. Each treatment was duplicated.

The urea-formaldehyde compound, used in the present study, was prepared in this laboratory following the method of Clark[5] using a buffered (pH 4.0), commercial 37 per cent formaldehyde solution preheated to 50°C and crystalline urea. The product was air-dried, ground to pass a 20 mesh sieve (B.S.S.) and finally stored in a well-stoppered bottle (Table 2). The availability index was determined according to the method suggested by Kralovec and Morgan[8].

* In Dist. Palamau, Bihar

TABLE 1—Soil Characteristics

Soil No.	*Location*	*Texture*	*Total Nitrogen, %*	*Organic Carbon (Walkley and Black's value), %*	*pH*
17	Netarhat (Bihar) Red upland, uncultivated	Clay	0.078	0.345	5.25
16	Ranchi (Bihar) Lowland	Clay loam	0.092	0.615	5.90
21	Barrackpore (W. Bengal) Jute Agricultural Research Farm	Alluvial sandy loam	0.087	0.480	7.00
24	Gwalior (M.P.)	Alluvial sandy clay loam	0.065	0.360	8.05
13	New Delhi, IARI farm	Alluvial sandy loam	0.071	0.285	8.30

TABLE 2—Some Characteristics of the Urea-form Material

1. Urea/Formaldehyde ratio	1.5:1
2. Total Nitrogen (TN), %	38
3. Cold Water-Insoluble Nitrogen (IN), %	24.2
4. $\frac{IN}{TN} \times 100$	63.7
5. Availability Index (AI)	45.9
6. Moisture, %	6.0

Results and Discussion

Urea-form: The data on the mineralization of urea-form and urea are given in Table 3, while Table 4 gives the data on the ammonium and nitrate-nitrogen accumulation from the two treatments after 1, 2, 4 and 14 weeks of incubation. The sum of ammonium and nitrate-nitrogen values in the treated soils minus the respective values in the untreated soils, expressed as the per cent of total nitrogen added, represents the per cent mineralization of the added nitrogen.

From Table 3, it can be seen that mineralization of the urea-form compound in alkaline and acid soils ranged from 2 to 21 per cent after one week, 13 to 60

TABLE 3—PER CENT MINERALIZATION OF UREA-FORM AND UREA IN SOILS & THE pH AT THE END OF EXPERIMENT

Period in weeks	Netarhat Clay	Ranchi Clay Loam	Barrackpore Sandy Loam	Gwalior Sandy Clay Loam	New Delhi Sandy Loam
	Urea-Form				
1	N.D.	21.00	20.44	2.20	8.72
2	44.08	60.00	36.50	33.44	13.04
4	54.04	65.56	54.00	43.36	N.D.
6	67.72	67.64	56.92	N.D.	42.44
10	62.52	69.04	66.24	55.64	49.56
14	40.48	71.48	70.44	61.24	67.76
(pH)	(5.95)	(4.60)	(6.00)	(7.05)	(7.45)
	Urea				
1	N.D.	70.00	34.52	37.52	65.20
2	78.20	100.00	55.92	46.28	N.D.
4	84.56	98.80	68.56	77.44	59.08
6	90.16	89.94	67.76	N.D.	61.52
10	74.16	90.04	68.72	61.24	65.60
14	50.16	81.88	68.56	76.44	72.76
(pH)	(6.00)	(4.65)	(6.20)	(7.15)	(7.50)

N.D.—Not Determined

per cent after 2 weeks and 61 to 71 per cent after 14 weeks' incubation respectively. It appears, therefore, that in general mineralization increases with decrease in the soil pH. This has also been observed by Winsor and Long[14]. It may also be seen that in all soils, except Netarhat clay, the urea-form material mineralized slowly but progressively throughout the incubation period. It is interesting to note that the highest per cent mineralization (ammonium+nitrate-nitrogen) was observed in the soil with initial pH of 5.9. This is in agreement with the observations of Kralovec and Morgan[8], Winsor and Long[14] and Basaraba[4], who noted that mineralization of urea-form fertilizers was more rapid in soils between pH 5.5 and 6.0 than in neutral or moderately alkaline soils.

In Netarhat clay, the mineralization increased upto 68 per cent in 6 weeks, thereafter the value falling gradually to 40 per cent at the end of the 14th week. This decreasing tendency in the percentage mineralization during the later stages of the experiment has also been noted in certain acid soils by Winsor and Long[14].

The data in Table 4 show that nitrate-nitrogen accumulated in all soils, except in Netarhat clay. It may also be observed that the alkaline soils accumulated more nitrate-nitrogen than the others. Thus accumulation of nitrate seems to depend on the initial pH of the soils, the value increasing with increasing pH. It is of interest to note that only traces of, or no nitrate accumulated in the Netarhat clay even after 14 weeks' incubation. This may be attributed either to the non-

TABLE 4—AMMONIUM AND NITRATE-NITROGEN ACCUMULATION

(*Expressed as per cent of applied nitrogen*)

Period in weeks	Netarhat Clay		Ranchi Clay Loam		Barrackpore Sandy Loam		Gwalior Sandy Clay Loam		New Delhi Sandy Loam	
	NH_4^+	NO_3^-	NH_4^+	NO_3^-	NH_4^+	NO_3^-	NH_4^+	NO_3^-	NH_4^+	NO_3^-
	Urea-Form									
1	N.D.	trace	21.00	nil	20.44	nil	2.20	trace	8.72	nil
2	44.08	trace	60.00	trace	29.90	6.60	8.48	24.96	5.32	7.72
4	54.04	nil	58.60	6.96	20.20	33.80	4.28	39.08	N.D.	38.40
14	40.48	nil	26.12	45.36	23.44	47.00	3.84	57.40	2.40	65.36
	Urea									
1	N.D.	trace	70.00	nil	34.52	nil	37.52	trace	65.20	nil
2	78.20	trace	100.00	nil	39.92	16.00	31.68	14.60	N.D.	nil
4	84.56	nil	85.88	12.92	29.44	39.12	21.00	56.44	11.84	47.24
14	50.16	nil	35.28	46.60	27.68	40.88	9.04	67.40	13.72	59.04

existence of nitrifying bacteria due to high initial acidity, or if present, their action might have been inhibited under such condition.

Appreciable quantities of ammonium-nitrogen remained at the end of the experiment in Netarhat clay (40 per cent), Ranchi clay loam (26 per cent) and Barrackpore sandy loam (23 per cent), whereas only very small quantities remained in the other two soils viz, Gwalior sandy clay loam (3.8 per cent) and New Delhi sandy loam (2.4 per cent). It appears, therefore, that oxidation of the ammonium-nitrogen to nitrate was quite rapid in the alkaline soils. The ammonium-nitrogen accumulation in the alkaline soils never exceeded 9 per cent, while in the acid soils more than 60 per cent accumulated in this form during 14 weeks' incubation.

It is seen from Table 3 that pH of all the soils, except Netarhat clay, treated with either urea-form or urea fell from the respective initial values after 14 weeks' incubation. This fall in pH is attributed to the accumulation of nitrate in these soils. The pH of the Netarhat clay fell from 6.45 after tenth week to 5.95 after fourteenth week. This was accompanied by a decrease in the ammonium-nitrogen content from 62.52 to 40.48 per cent without any accumulation of nitrate. However, the final pH of the soil was higher than the initial value which may be due to ammonium nitrogen still persisting after 14 weeks' incubation.

Urea: The data in Table 3 show that the mineralization of urea was virtually complete within the first few weeks of incubation. The mineral nitrogen recovery was greater in the acidic soils than others probably due to some loss of ammonia by volatilization in the latter soils. Incidentally, highest mineralization occurred in the Ranchi clay loam with initial pH 5.90. This has also been observed in the urea-form treatment. However, the mineral nitrogen content tended to decrease in the two acid soils, viz, Ranchi clay loam and Netarhat clay after the fourth and tenth weeks respectively. Nitrate-nitrogen accumulated in all soils, except in Netarhat clay and the values were higher in the alkaline soils (Table 4). In the Netarhat clay, the mineralization increased up to the sixth week and subsequently tended to decrease. This decrease in the mineral-nitrogen content during the last 4-week period was accompanied by a fall in pH from 6.50 to 6.00, and yet the final pH was higher than the initial value. Similar trend was also observed in the urea-form treatment as discussed earlier. In all other soils, the pH after 14 weeks' incubation dropped from the respective initial values, evidently due to accumulation of nitrate. Appreciable quantities of ammonium-nitrogen remained in the acid soils at the end of the experiment.

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Studies on the Soil & Leaf Applications of Various Nitrogenous Fertilizers

By

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In a field trial with potato, it has been noted that soil application of ammonium nitrate, ammonium bicarbonate and a 50-50 mixture of the two is superior to their corresponding leaf applications. A mixture of ammonium bicarbonate and ammonium nitrate might have a greater fertilizer value than either of them applied alone.

Introduction

Potato is one of the important crops grown in India. It is cultivated annually in an area of about 7 lakh acres, concentrated mostly in the U.P., Bihar, W. Bengal and Assam. It is a major vegetable in our diet, and produces more food per unit area than any other vegetable crop. Obviously, any effort which may increase its production is bound to affect the problem of human food, health and economy much more intimately than a similar effort in any other direction.

The phenomenon of spray fertilization has long been known to the agriculturists. Only in recent years, the potentiality of foliar absorption has been established[1]. Under the *akiochi** soil conditions in Japan, Nagai[2] obtained 15.22 per cent increase in the yield of rice, using urea sprayed at the rate of 17.5 kg/ha in the form of a 2 per cent solution with a suitable sticker.

The comparison of the responses of potato to different sources of nitrogen at 50 and 100 lbs/acre was studied in India[3] during 1958-59. In Bihar, the response of potato to calcium ammonium nitrate was of lower order as compared with that of urea and ammonium sulphate nitrate (ASN). In W. Bengal the average response to different sources of nitrogen did not differ significantly from one another. Similar were the cases in Orissa, H.P. and the U.P. It was observed in the previous experiments[4] that for *Aus* paddy ammonium bicarbonate is a better fertilizer than ammonium sulphate on equal nitrogen basis. The present investigation was made to study the relative merits of ammonium bicarbonate, ammonium nitrate and a fifty-fifty mixture of the two on the growth and development of potato plants. Comparison was also made between soil and spray applications of the fertilizers.

* A type of Japanese soil

Experimental

Materials & Methods: The experiment was undertaken at the Fertilizer Trial Station of this Division at Sindri. Soil homogeneity was ensured from the uniformity of the standing crop of potato. Special care was taken in respect of the uniformity of seeds, planting, fertilizer application, irrigation, drainage, etc.

The area was ploughed uniformly with a disc plough, harrowed and laddered uniformly without a break leaving the headland completely outside the experimental area. The soil type being sandy loam, an ideal tilth for potato crop was obtained throughout.

The variety of potato selected was Royal Kidney as it is well sensitive to fertilizer treatments. 1-1.5 oz. seed tubers were cut so that there was at least one eye in each cut-tuber, soaked in Agallol and planted in trenches on 14.12.1964.

Ammonium bicarbonate and ammonium nitrate were used as sources of nitrogen. A constant dose of nitrogen, i.e. 20 lbs. N/acre, was used both for soil and leaf applications.

All the fertilizers were sampled and analysed before application in the manner given in Tables 1 and 2.

TABLE 1—YIELD OF POTATO TUBERS/PLOT, KG.

Treatments	*Block I*	*Block II*	*Block III*	*Average Yield*
O(L)	1.15	1.20	1.25	1.20
O(S)	1.15	1.32	1.20	1.22
ABN(L)	1.30	1.80	1.25	1.45
ABN(S)	1.40	2.80	1.60	1.93
AN(L)	1.35	1.25	1.70	1.43
AN(S)	0.90	2.00	1.80	1.56
AB(L)	1.40	1.70	1.40	1.50
AB(S)	1.45	1.70	1.70	1.61

TABLE 2—NUTRIENT CONTENT OF THE POTATO TUBERS, %
(*Dry Matter Basis*)

Treatments	*N*	P_2O_5	K_2O
O(S)	1.10	0.41	1.70
O(L)	1.09	0.41	1.70
AN(S)	1.23	0.44	1.88
AN(L)	1.28	0.46	2.03
AB(S)	1.23	0.42	1.75
AB(L)	1.29	0.46	2.03
ABN(S)	1.20	0.43	1.82
ABN(L)	1.28	0.46	1.94

Folidol E-605 at the rate of 0.03 per cent was applied on 21.1.65 as a preventive measure against insect attacks. Phytolan was applied on 19.1.65 and 28.1.65 to prevent the attack of blight.

The methods used for the chemical analysis of the potato tubers were the same as those used in the previous experiments[4].

Procedure: Randomized block design with three replications was used for these experiments, the net area of the plots being 12 ft.×6 ft with 4 rows in each plot. The spacing between the rows was 1.5 ft., and the same between hills which were 16 per row was 9 in. Only two middle rows were harvested leaving two border rows as discards.

The planting was done in trenches and completed within the same day keeping the number of rows, hills and spacings constant for each plot. The seed tubers were then covered uniformly with loose fine soil making small ridges.

Soil Applications: Soil application was made twice—once on 23.1.65 and the other on 6.2.65. The quantity of fertilizer was dissolved in water and applied to soil (Table 1). To avoid scorching of the lower leaves more 'fresh' water was also given to wash the leaves and facilitate the rootward movement of the nutrients. The same quantity of water was applied in the control plots.

A 5 per cent solution of the fertilizers was prepared and sprayed uniformly over the plants maintaining the height of the nozzle steady. The control plots were also sprayed with fresh water. Altogether four sprays were given, viz. on 23.1.65, 30.1.65, 6.2.65 and 13.2.65.

TABLE 1—SCHEDULE FOR ONE SOIL APPLICATION

Treatment	*Abbreviation*	*Quantity of Fertilizers, g.*	*Quantity of Water, gal.*
Ammonium Bicarbonate	AB	44.15	1
Ammonium Nitrate	AN	28.85	1
Ammonium Bicarbonate +Ammonium Nitrate	ABN	36.5 (AB 22.07+ & AN 14.42)	1

TABLE 2—SCHEDULE FOR ONE SPRAY APPLICATION

Treatment	*Quantity of Fertilizer, g.*	*Quantity of Water, ml.*
Ammonium Bicarbonate	22.07	441
Ammonium Nitrate	14.42	288.4
Ammonium Bicarbonate +Ammonium Nitrate	16.80 (AB 11.03+AN 7.21)	364.8

Effect of Fertilizers on the Growth: Scorching effects were noticed on the leaves on the days following each spray. These effects increased up to the 3rd day after spraying, the maximum scorching being with ammonium bicarbonate, the minimum with ammonium nitrate, and intermediate with treatment of the mixture of the two. The colour of the leaves improved remarkably.

Results and Discussions

Fig. 1 computed from Table 1 presents the yield of tubers obtained from different treatments. It is quite apparent that in general the tuber yield from soil

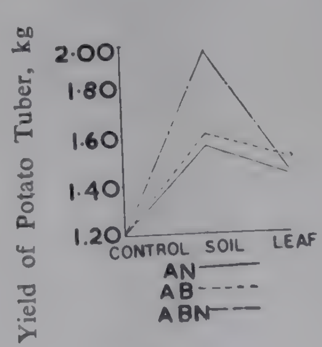

Fig. 1

treatments was more than that from leaf treatments though not very remarkable in case of the treatments with ammonium nitrate and ammonium bicarbonate. The mixture of ammonium bicarbonate and ammonium nitrate seems to be superior to either of the two applied singly to soil.

In case of leaf application it appeared that all the three sources of nitrogen were more or less equally effective in encouraging tuber yield.

Nutrient content of potato tubers on dry matter basis is given in Table 2.

Fig. 2 shows the percentage of nitrogen in the potato tubers of the soil and leaf-treated plants. Considering the effect of all three sources of nitrogen, the leaf-treated plants had higher percentages of nitrogen than the soil-treated ones.

In the soil-treated plants, the nitrogen percentage value of the tubers of a 50-50 mixture of ammonium bicarbonate and ammonium nitrate was less than in the cases of other two sources which were at par. In the leaf treatments, the uptake of nitrogen did not differ widely and all three sources had similar values.

Fig. 3 shows that the percentage of P_2O_5 in potato tuber was always higher in leaf treatments than the soil treatments. Of course, some variations within the sources were noticed in the soil treatments, such as the uptake of P_2O_5 was highest in ammonium nitrate treatment, lowest in ammonium bicarbonate treatment, while the value was intermediate in the treatment with 50-50 mixture of the two.

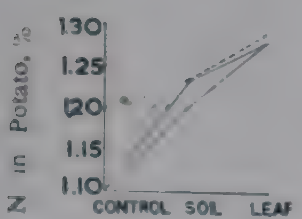

Fig. 2

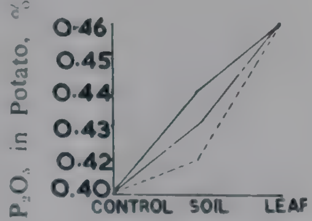

Fig. 3.

In case of leaf treatments the percentages of P_2O_5 did not vary with different sources (Fig. 4).

Similar trend was also noticed in the case of the

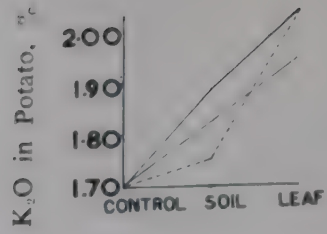

Fig. 4

percentage of potash except in the case of the mixture of ammonium bicarbonate and ammonium nitrate. In this case, leaf treatments resulted in lower percentages of K_2O than the two other sources (Fig. 4).

It is quite apparent from the above findings that in the case of leaf treatments as the yield decreases the percentages of N, P and K in the tuber increases.

A reverse trend was noticed in the case of soil treatments. The highest yield was obtained with the mixture of ammonium bicarbonate and ammonium nitrate. Probably because of the limited indigenous resources of nitrogen the percentage of nitrogen in tubers decreased in this treatment.

In the soil treatments, the uptake patterns of P_2O_5 and K_2O in all three forms were somewhat irregular, signifying that these components were not limiting in the soil.

In the case of leaf treatments there was very little variation in the yield and in the uptake of N, P & K in tubers with the different sources.

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Hygroscopicity of Fertilizers

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The relative rates of moisture absorption by various fertilizers have been determined under static conditions. An attempt has been made to calculate critical relative humidity of the multi-nutrient mixtures and some of the nitrogenous fertilizers from moisture absorptions values. Calculated critical relative humidity values so obtained are in fair agreement with those given in the literature, obtained from vapour pressure data. Theoretical implications involved are discussed.

Hygroscopicity is the tendency of a substance to absorb moisture from the atmosphere. A salt absorbs moisture when the vapour pressure of its saturated solution is less than the partial pressure of vapour in the atmosphere. Many of the fertilizers, being hygroscopic, need protection from the ambient humidity, for which air-conditioning of silo, where the fertilizers are stored in bulk, is generally the first step. The fertilizers are then bagged in moisture-proof bags prior to their despatch. At places, where humidity is very high, parts of the plant where granules are crushed and sieved are also air-conditioned. This keeps the plant free from slush caused by spillage of fertilizers.

From the industrial standpoint it is necessary to know whether a fertilizer would absorb moisture under the prevailing conditions of humidity and temperature, and if it does then what are the conditions of humidity and temperature to be maintained in silo, and the type of packaging required for bagging the finished product. Hygroscopicity of a fertilizer is very conveniently designated by its Critical Relative Humidity, which is the ratio in percentage of vapour pressure of saturated solution to the vapour pressure of saturated air at the same temperature. If the relative humidity of atmosphere is greater than the critical relative humidity of the fertilizer then only the fertilizer would absorb moisture. Critical relative humidity of most of the fertilizers have been determined by Adams and co-workers,[1, 2] and the values of some of the binary mixtures of fertilizers are also known. All of these values have been determined by vapour pressure measurements.

Critical relative humidity is an equilibrium property of the system. It is not directly related to the rate of moisture absorption, except that it can be inferred that under similar conditions fertilizers of relatively low critical relative humidity will absorb moisture more rapidly than those of high critical relative humidity. The relative rate of moisture absorption can only be ascertained by measuring the weight increase of samples exposed to controlled humidity under similar conditions. In the present paper an attempt has been made to evaluate the critical relative humidity from moisture absorption values determined under static conditions in the laboratory, and the theoretical implications involved are discussed.

Previous studies on relative hygroscopicity have revealed various interesting features; the rate of moisture absorption does not change with change in particle size and is governed by surface area exposed rather than on the amount of sample[3]. Furthermore, it was found that this rate was considerably less under static conditions. Lindsay[4] and others have raised objection to making moisture absorption experiments in stagnant atmosphere. Fertilizers are liable to absorb moisture in silo, where the product is stored in bulk and later in warehouses where the bagged product is kept. Under both these conditions, the atmosphere to which fertilizers are likely to be exposed simulate stagnant rather than unconfined condition. Hence, moisture absorption experiments carried out under static conditions may in fact be of greater relevance in the present context than the experiments done under continuous flow conditions.

Experimental

Various fertilizer samples were granulated to 8 to 10

mesh (B.S.S.) size, and 3 g. of each sample dried on a *petri* dish kept in a desiccator containing water (R.H. 100%). The increase in weight of the sample was noted at 2 and 5 hr. intervals (Table 1).

Discussion

The rate of mass transfer can be written in the form›

$$\text{Rate} = \frac{\text{driving force}}{\text{Resistence}} \times \text{Area}$$

A salt absorbs moisture when the vapour pressure of moisture in the atmosphere exceeds the vapour pressure of its saturated solution. The driving force, therefore, can be taken as p_o-p where p_o and p are the vapour pressure of atmosphere and saturated solution respectively. More convenient form will be to express in terms of relative humidity, i.e. h_o-h, where h_o and h are the relative humidity of atmosphere and critical relative humidity of the salt respectively. Under static condition of moisture rate determinations, the thickness of stagnant air film may become so large that rate of diffusion of moisture through this film may become rate determining. Therefore, resistance in the present case may be taken as the diffusional resistance offered by a laminar film of stagnant air surrounding the particles. Other factors, such as diffusion of salt in solution and of moisture through air, as well as the resistance offered by solution surrounding the particles may be neglected. Area on which the driving force acts can be taken as the surface area of the salt exposed to the confined humid atmosphere.

The rate of moisture absorbed can be expressed by the following equation: $Q=KA\ (h_o\text{-}h)$
where Q is the amount of moisture absorbed per hr., g.;

A=the surface area of the sample exposed, cm^2;
K=the rate coefficient of absorption of moisture, which includes the resistance offered to the mass transfer;
h_o=the relative humidity of confined air;
h=the critical relative humidity of the fertilizer.

Hygroscopicity of fertilizers is known to increase with increase in temperature. The increase in rate of moisture absorption with increasing temperature may arise largely on account of increase in the driving force h_o-h on account of decrease in the values of h with increase in temperature as shown below. The coefficient, K, will also change as the diffusional resistances tend to decrease with increase in temperature. Critical relative humidity of most of the fertilizers fall with increase in temperature. The decrease is more in the case of urea and ammonium nitrate (or calcium ammonium nitrate).

Fertilizers	*Critical Relative Humidity, h, Temperature, °C*				
	15°	20°	25°	30°	40°
NH_4NO_3	69.8	66.9	62.7	59.4	52.5
$CO(NH_2)_2$	79.9	80.0	75.8	72.5	68.0
$(NH_4)_2SO_4$	79.3	81.0	81.8	79.2	78.2

In the present series of experiments, the amount of fertilizer samples of 8-10 mesh (B.S.S.) size taken was just sufficient to completely cover the *petri* dishes of identical size in order to ensure that the surface area exposed in every case was the same. The samples were exposed to the same humidity and temperature was fairly constant. Taking 59.4 per cent at 30°C as the critical relative humidity of ammonium nitrate, the critical relative humidities of other fertilizers were determined by the following equations.

$$Q_1=KA\ (h_o\text{-}h_A) \qquad .. \quad \text{(i)}$$
$$Q_2=KA\ (h_o\text{-}h_x) \qquad .. \quad \text{(ii)}$$

Where h_A is the critical relative humidity of ammonium nitrate, h_x the critical relative humidity to be determined, Q_1 and Q_2 are the amount of moisture absorbed in 2 or 5 hr. h_o is the relative humidity of the atmosphere to which the samples are exposed. Equation (1) and (2) lead to

$$h_o = \frac{Q_1 h_x - Q_2 h_A}{Q_1 - Q_2} \qquad .. \quad \text{(iii)}$$

h_x values, calculated from the above equation, appears to be in agreement with some of the values given in the literature as determined from vapour pressure data. Only in the case of monoammonium phosphate urea mixture the critical relative humidity calculated from vapour pressure data is considerably higher than obtained from moisture absorption values.

When two fertilizers are mixed together, any of the following may happen:

1. Mixed fertilizers may become more hygroscopic than any of the constituents. The examples are: urea+ammonium nitrate, urea+ammonium sulphate, ammonium nitrate+monocalcium phosphate, etc.
2. Hygroscopicity of mixed product may correspond to that of the more hygroscopic component viz. monoammonium phosphate+ammonium nitrate and ammonium nitrate+potassium nitrate.
3. Hygroscopicity of mixed fertilizers is less than

that of a more hygroscopic component. This is more common in the case of a double salt formation, viz. $(NH_4)_2SO_4.2NH_4NO_3$; $Ca(NO_3)_2 4CO(NH_2)_2$; $NH_4NO_3.Ca(NO_3)_2.2H_2O$.

4. Hygroscopicity may change as a result of double decomposition reactions, viz. NH_4NO_3+KCl leads to less hygroscopic $NH_4Cl+KNO_3$; $(NH_4)_2SO_4+KCl$ forms more hygroscopic NH_4Cl.

The results indicate that a mixture of urea with monoammonium phosphates fall into first category, MAP+urea being more hygroscopic than DAP+urea although critical relative humidity of MAP is higher that that of DAP (Table 1). Furthermore, change in mole ratio of MAP/urea from about 1 to 3 does not decrease the hygroscopicity of the mixed fertilizer. This is not surprising as the hygroscopicity depends on the vapour pressure of solution saturated with respect to both salts. Therefore any constituents present in quantities larger than required for saturation would give the same order of hygroscopicity. Slight difference in the rate may, however, be noticeable as the proportion of more hygroscopic component is progressively decreased on account of decrease in rate of dissolution occurring as a result of reduced area of contact between solution and dissolving phase. A mixture of monoammonium phosphate with ammonium sulphate (16-20-0) is considerably less hygroscopic than other fertilizer mixtures and, according to our experience, behaves exceedingly well even under adverse climatic conditions.

When ammonium sulphate-nitrate is mixed with superphosphate in a proportion to give nutrient ratio 2-1-0, the resulting product is more hygroscopic than ammonium sulphate-nitrate. This may be due to reaction between ammonium sulphate and monocalcium phosphate, and the resultant product is a mixture of monoammonium phosphate, ammonium nitrate, ammonium sulphate and calcium sulphate. It falls in the category 2 (mentioned above) and its hygroscopicity values correspond to these of ammonium nitrate. The water-soluble phases of nitro-phosphate (50 per cent water-soluble) also consist mainly of ammonium nitrate and diammonium phosphate, and therefore nitro phosphate is as hygroscopic as ammonium nitrate. In spite of the high proportions of water insolubles present in nitro phosphate and calcium ammonium nitrate, these fertilizers are as hygroscopic as ammonium nitrate, because during the process of drying the inert particles as well as the granules, as a whole, are coated with a film of soluble components of the fertilizer and the surface area exposed is high.[5]

The impurities present in fertilizer-grade ammonium

TABLE 1—HYGROSCOPICITY AND CRITICAL RELATIVE HUMIDITY OF FERTILIZERS

Fertilizers	*Nutrient Content*	*Cumulative Moisture absorbed at 30±1°C Exposed to 100% R.H.*				*Critical Relative Humidity (in %) Calculated from Equation (iii), h_x*			*Critical Relative Humidity (in %) at 30°C from vapour pressure data, h_x*
		2 hr		*5 hr*		*2 hr*	*5 hr*	*Average*	
		g.	%	*g.*	%				
Ammoniam nitrate	35-0-0	0.090	3.0	0.210	7.0	—	—	—	59.4
Calcium ammonium nitrate	20.5-0-0	0.093	3.1	0.216	7.2	58.0	58.2	58.1	—
Ammonium sulphate-nitrate	26-0-0	0.081	2.7	0.180	6.0	63.4	65.2	64.3	62.3
Urea	46-0-0	0.060	2.0	0.141	4.7	72.9	72.7	72.8	72.5
Nitro-phosphate (50% water soluble)	13-13-0	0.093	3.1	0.213	7.1	58.0	58.8	58.4	—
Monoammonium phosphate (MAP)+Urea	18.36-0	0.099	3.3	0.237	7.9	55.3	54.2	54.7	65.2
Monoammonium phosphate (MAP)+Urea	32-16-0	0.102	3.4	0.243	8.1	54.0	53.0	53.5	65.2
Monoammonium phosphate (MAP)+ $(NH_4)_2SO_4$	16-20-0	0.054	1.8	0.132	4.4	75.6	74.5	75.0	75.8
Diammonium phosphate (DAP)+Urea	28-28-0	0.084	2.8	0.198	6.6	62.6	61.6	62.1	—
Ammonium sulphate+Superphos.+KCl	8-8-8	0.063	2.1	0.144	4.8	71.3	72.1	71.7	—
Ammonium sulphate-nitrate+Superphos.	14-7-0	0.093	3.1	0.207	6.9	58.0	59.9	58.9	—
Ammonium chloride	25-0-0	0.063	2.1	0.144	4.8	71.3	72.1	71.7	(77.2)
Ammonium chloride (pure)	26.2-0-0	0.054	1.8	0.129	4.3	75.6	75.0	75.3	77.2

chloride made it as hygroscopic as urea. Pure ammonium chloride is, however, less hygroscopic, and its critical relative humidity calculated from moisture absorption data is nearer to the values recorded in the literature.

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Ultraviolet Spectrophotometric Method of Estimation of Biuret in Urea

By

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A method has been developed for the estimation of biuret in fertilizer-grade urea by studying absorption in ultraviolet region with the help of a quartz spectrophotometer. After comparing with a standard method, the present one has been found more suitable in respect of speed and accuracy.

Introduction

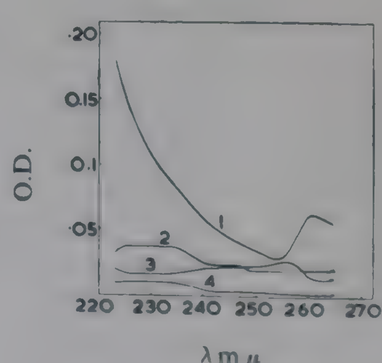
Fertilizer-grade urea invariably contains a small amount of biuret which is poisonous to some plants. Therefore, biuret has to be estimated accurately and controlled during urea manufacture. It is an usual procedure now-a-days to estimate small quantities of biuret in urea by forming a coloured biuret complex in presence of an alkali and then measuring the intensity of the colour by means of a spectrophotometer[1-3]. This procedure requires quantitative conversion of biuret into the coloured complex and has not been found very suitable for cases with low amounts of biuret—less than 0.5 per cent—in urea. The present method which does not require any complex formation, is based on an accurate determination of selective ultraviolet absorption of biuret in standard alkaline and buffer solutions.

It has been reported in literature[4] and also verified by us that biuret in 0.1 N solution of sodium hydroxide has a considerable absorption at 225 m μ and a peak at 260 m μ (Fig. 1). Urea, on the other hand, in such a solution has no appreciable absorption. Further experiments show that urea and biuret both have negligible absorption in a buffer solution of pH 9. Therefore, the above two wavelengths were chosen for the present investigation.

Absorbancy A of a mixture containing several components at a given wavelength can be written down[5] from Beer's law as,

$$A=b(a_1c_1+a_2c_2+a_3c_3+\dots\dots\dots) \qquad (1)$$

where a_1, a_2, etc. are absorptivity of individual constituents in l./g. cm, c_1, c_2, c_3, etc., concentration of the constituents in g./l. in the solution, and b the corrected path length in cm. In the present case if C be the concentration of biuret in g./l. in 0.1 N sodium hydroxide



Curve 1... 0.005 g./l. of Biuret in 0.1 N NaoH
Curve 2... 0.1 g./l. of Urea inpH 9 buffer
Curve 3... 0.005 g./l. of Biuret inpH 9 buffer
Curve 4... 0.1 g./l. of Urea in 0.1 N NaoH

Fig. 1—U. V. Spectra of Biuret and Urea

solution and X the concentration of impurity present in the solution, the optical density at 225 m μ can be put as,

$$A_1 = C\,\epsilon_1 + X\epsilon'_1$$

Similarly, at 260 mμ,

$$A_2 = C\,\epsilon_2 + X\epsilon'_2$$

where ϵ_1 and ϵ_2 are extinction co-efficients of biuret in 0.1 N sodium hydroxide at 225 and 260 m μ and ϵ'_1 and ϵ'_2 are average extinction co-efficients of impurities in the solution at those two wavelengths.

Therefore, for difference of absorbance[6] we have

$$\Delta A = A_1 - A_2 = C\Delta\epsilon + X\Delta\epsilon' \ldots\ldots\ldots \quad (2)$$

Thus the optical densities obtained in alkaline solution alone would not lead to the correct determination of concentration of biuret because the presence of impurities may have contributed to the absorption in sodium hydroxide. However, in a buffer solution of pH 9, for the optical densities of the mixture containing biuret and urea with impurities,

$$A'_1 = X\,\epsilon''_1 \text{ at } 225 \text{ m}\mu$$

$$\text{and } A'_2 = X\,\epsilon''_2 \text{ at } 260 \text{ m}\mu$$

where ϵ''_1 and ϵ''_2 are the average extinction co-efficients of the impurities at the 225 and 260 m μ respectively. then have,

$$\Delta A' = A'_1 - A'_2 = X\Delta\epsilon'' \ldots\ldots\ldots \quad (3)$$

Eliminating X between (2) and (3), we have,

$$C = \frac{\Delta A}{\Delta\epsilon} - \frac{\Delta A'}{\Delta\epsilon''}\,\frac{\Delta\epsilon'}{\Delta\epsilon} \ldots\ldots\ldots\ldots \quad (4)$$

Now at the given pair of wavelengths, the factors $\frac{1}{\Delta\epsilon}$ and $\frac{\Delta\epsilon'}{\Delta\epsilon''\Delta\epsilon}$ depend somewhat on the instrument and the given set of experimental conditions but are independent of the concentration of biuret; these may therefore be regarded as constants. These are determined experimentally by measuring optical densities at these two wavelengths with a set of solutions of known concentration of biuret in urea and are found to be 0.036 and 0.032 respectively. The working equation for biuret estimation therefore reduces to,

$$C\,(\text{g./l.}) = 0.036.\ \Delta A - 0.032.\ \Delta A' \ldots\ldots \quad (5)$$

Experimental

Measurements were taken at 225 and 260 m μ with two solutions, one in 0.1 N sodium hydroxide and the other in a buffer solution of pH 9 (mixture of boric acid, potassium chloride and sodium hydroxide in requisite amounts). A Russian make spectrophotometer, type C ϕ 4, was used with an antimonic-caesium phototype cell using hydrogen lamp as the source. The cell constant for 1 cm. quartz cell used in the experiment was also determined to evaluate the correct value of optical density. Urea and biuret used were all of AnalaR (BDH) variety, and each of them had been re-crystallized three times in the laboratory before use. Prepared samples of urea (0.1 g./l.) containing different but known percentages of biuret ranging from 0.5 to 5 per cent have been analysed along with a commercial grade urea.

Results and Discussion

The results of the measurement are presented in Table 1 wherein columns 3 and 2 bring out a comparison between the experimentally observed and calculated values of concentrations, while column 5 shows those values as measured by the standard copper biuret complex method[1]. It will be seen that the present method gives a closer agreement.

TABLE 1

Sample No.	*% of Biuret Taken*	*% of Biuret Observed*	*Error*	*% of Biuret by Standard Copper Complex Method*
I	0.5	0.52	+0.02	0.45
II	1.0	0.99	−0.01	0.91
III	1.5	1.40	−0.10	1.45
IV	2.0	2.19	+0.19	1.90
V	2.5	2.59	+0.09	2.64
VI	3.0	3.12	+0.12	3.13
VII	5.0	4.91	−0.09	5.11
VIII	Commercial	1.42		1.45

It may be observed that the working formula is truly based on the assumption of a single impurity component in urea-biuret mixture. Although a number of impurities might be present, their concentration as well as absorption are negligibly small. A simplification has, therefore, been introduced by taking a single value for the average extinction coefficient. The two solvents and the wavelengths for the estimation were selected by the most suitable values as determined experimentally (Fig. 1). Conformity to Beer's law was found very satisfactory up to the range of 5.0 per cent using 1 cm. quartz cell.

As regards the advantages and suitability of this method for the estimation of biuret in urea, it may be pointed that absorption of the solution is measured directly by it and that a very small amount of sample is required. It is very simple, rapid and accurate, and has been

found much suitable for very low amounts of biuret.

Acknowledgements

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Ammonia Loss During Storage of Calcium Ammonium Nitrate

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Loss of ammonia during storage of calcium ammonium nitrate at Nangal was found excessive. This has been shown to be due to the high reactivity of one of the limestone samples containing higher percentage of magnesium. The possible cause of this high reactivity has been indicated. Alkalinity determination of the aqueous extract is found to be a convenient and reliable index for the reactivity of limestone in the context of ammonia loss during storage. A new mechanism of ammonia loss has been suggested which explains the observed facts. The loss appears to be dependent on the soluble calcium/water ratio.

Introduction

The manufacture of calcium ammonium nitrate involves mixing of hot ammonium nitrate melt with pulverized limestone. Under these conditions some ammonia is invariably lost on account of following reactions.[1]

$$2NH_4NO_3 + CaCO_3 \rightleftharpoons (NH_4)_2\,CO_3 + Ca(NO_3)_2$$
$$(NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$$

The extent of ammonia loss can be ascertained by the estimation of calcium nitrate content in the product: each mole of calcium nitrate formed is equivalent to two moles of ammonia lost. Normally the loss is to the extent of about 1-2 tons of ammonia per thousand tons of the product, and it is, to a large extent, unavoidable unless the whole operation of mixing and granulation is carried out in a closed system and the evolved ammonia is recovered by scrubbing it with a weak nitric acid solution. In practice this is not done. Losses have been found to depend on various factors, viz. temperature and concentration of the melt, particle size of limestone and ammonium nitrate-limestone ratio.[2] The most important factor is the temperature of the melt and the losses increase rapidly with increase in temperature. These losses are also dependent on type of limestone used and stated to be more with high calcium limestone than with dolomitic limestone[3].

There are, at present, two plants producing CAN in India—one at Nangal in Punjab and the other at Rourkela in Orissa. At both these plants, limestone is used as a diluent for the manufacture of CAN with 20.5 per cent nitrogen. Ammonia losses in the silo at Nangal was found to be excessive. The concentration of ammonia in the atmosphere inside the silo exceeded health hazard limit, viz. it is 50 ppm for 8 hr exposure, thus causing much inconvenience to all concerned especially the scraper operators. Furthermore, these losses in-

crease during monsoon months. There was no such problem at Rourkela, where the concentration of gaseous ammonia inside the silo was much below the health hazard limit. It may be mentioned that the air-conditioning systems provided for the dehumidification inside the silo were not functioning when the author (S. V.) visited these plants.

Results and Discussion

The increase of ammonia concentration in the silo at Nangal during monsoon period indicates that the loss of ammonia is related to the moisture content of the product, but that it is not the only cause is evident from the fact that no such problem was encountered at Rourkela where humidity is high all the year round and goes upto 90 per cent during monsoon. Since the limestones used at both the places were from different sources, it was suspected that the fault probably lay with the limestone used at Nangal. No reference could be found in the literature on the reactivity of limestone in relation to the ammonia losses during manufacture or storage of CAN.

The diluent used at Nangal is a mixture of limestones from the quarries of Punjab, Rajasthan and north-western U.P. Limestones used in both the plants were analysed.

The aqueous alkalinity is determined by titrating the twice-filtered aqueous extract of 5 g. sample of powdered limestone with a standard acid (Table 2). In each case the sample is extracted with 30 ml. of CO_2-free distilled water.

Table 1—Analysis of Limestone, %

Samples	*Loss on Ignition*	*CaO*	*MgO*	*SiO_2 and other HCl In-solubles*	*R_2O_3 (R=Fe and Al)*
A (From Nangal)	43.0	51.9	1.1	2.7	0.9
B ,, ,,	42.1	49.3	2.9	3.7	1.4
C ,, ,,	42.7	46.8	4.9	4.0	1.2
D ,, ,,	42.2	44.6	6.4	5.0	1.6
E ,, ,,	42.2	48.5	3.4	4.1	1.3
F ,,	43.6	32.7	16.1	5.1	2.3
G (From Rourkela)	43.1	50.3	1.1	3.5	1.4
H ,, ,,	43.3	50.4	1.5	3.4	1.3
I ,, ,,	43.0	49.0	2.8	3.5	1.2

The estimation of Ca^{2+} and Mg^{2+} together is done by EDTA using Eurochrome T as the indicator, while Ca^{2+} is estimated by Murexide. These estimations indicated that the alkalinity is due solely to the dissolved calcium carbonate.

The results further show that the pure calcium carbonate gives less alkalinity than the samples examined. The sample F gave unusually high alkalinity in aqueous extract (Table 2). Calcium ammonium nitrate prepared in the laboratory with this sample was found to evolve ammonia even at ordinary temperature, which increased when the sample was kept under humid atmosphere. The increase of temperature had similar effect and the nitro-limestone F continued to lose weight when dried at 60°C. Similar losses, though to a lesser extent, were observed with sample D. Both these samples were from Rishikesh (U.P.). The losses of ammonia with CAN prepared from other samples of limestones were found to be negligible. These observations indicate that the aqueous alkalinity determinations are in some way related to the tendency of limestone to evolve ammonia from CAN. This may be explained as follows.

Table 2—Aqueous Alkalinity of Limestone

Sample	*Vol. of N/51 H_2SO_4 Required for Neutralization, ml.*
A	0.30
B	0.35
C	0.35
D	0.55
E	0.25
F	0.95
G	0.30
H	0.20
I	0.25
Pure $CaCO_3$	0.10

The solubility of calcium carbonate in boiled CO_2-free distilled water is 0.0145 g./l. at 17°C[4]. Kuster showed that in an aqueous solution calcium carbonate is not only ionized but also hydrolysed to the extent of more than 80 per cent of dissolved calcium carbonate[5]. This leads to the alkalinity of CO_2-free water extract of calcium carbonate. Alkalinity of aqueous extract may, therefore, be taken as a measure of the extent to which limestone is hydrolysed in water i.e. of the reactivity of limestones towards water. There are two possible mechanisms according to which the loss of ammonia occurs during storage of CAN. The first is the reaction between ammonium nitrate and calcium carbonate leading to the formation of ammonium carbonate as an intermediate product, which dissociates slowly into ammonia, carbon dioxide and water. This is the accepted

machanism. The second possibility is the hydrolysis of calcium carbonate by water. Calcium hydroxide so formed reacts with ammonium nitrate to evolve ammonia. The authors favour the latter and have suggested the following mechanism, which does not preclude the possibility of the other mechanism operating simultaneously or from becoming more significant at high temperatures during the manufacture of CAN.

$$\underset{\text{solid}}{CaCO_3} \rightleftharpoons \underset{\text{dissolved}}{Ca^{2+}CO_3^{2-}} \quad \text{(i)}$$

$$Ca^{2+}CO_3^{2-} \cdot 2H_2O \rightleftharpoons Ca(OH)_2 + H_2O + CO_2 \quad \text{(ii)}$$

$$Ca(OH)_2 + 2NH_4NO_3 \longrightarrow Ca(NO_3)_2 + 2NH_3 + 2H_2O \quad \text{(iii)}$$

Overall reaction is given by

$$2NH_4NO_3 + CaCO_3 \rightleftharpoons 2NH_3 + CO_2 + H_2O + Ca(NO_3)_2 \quad \text{(iv)}$$

From the above mechanism, it is clear that in presence of ammonium salts calcium hydroxide formed as a result of reaction (ii) will react with ammonium nitrate and shift its equilibrium to the right i.e. causing an increased hydrolysis. This explains the decomposition of calcium carbonate in presence of ammonium salts[6]. The influence of water on hydrolysis of calcium carbonate is evident and the losses will increase with increase in moisture content of the product. According to the above mechanism, addition of calcium ions should suppress ammonia liberation by shifting the equilibrium of reaction (i). This has been found to be the case. When calcium carbonate or limestone was added to the saturated solution of ammonium nitrate, a strong smell of ammonia was felt. The evolution of ammonia was considerably minimized when a sufficient amount of soluble calcium salts, viz. a nitrate or chloride, was present along with ammonium nitrate. This observation is significant as it points out that calcium nitrate present in CAN serves useful purpose and may be instrumental in suppressing further dissociation of CAN during its storage. This may explain the decrease in ammonia loss, noticed by Pawlikowski[7] when a small quantity of gypsum was added along with limestone. Here gypsum provides calcium ions and is also capable of fixing ammonia as ammonium sulphate. The by-product chalk is expected to be less reactive as it contains gypsum as an impurity.

This has been found to be the case[8]. This repression of ammonia evolution would depend on soluble calcium/water ratio. For example, in the case of CAN, the fresh product may contain 0.8 per cent of calcium nitrate and one per cent water. The moisture present will be saturated with respect to ammonium nitrate and undersaturated with respect to calcium nitrate. Calcium nitrate/water ratio in this case is 0.8. Any absorption of moisture by CAN will decrease the ratio and thus accentuate the loss of ammonia. The losses will continue till the optimum ratio is reached. At a particular temperature, this ratio will be a variable factor depending on the reactivity of limestone. The results indicate that the sample F gives unusually high alkalinity, and its magnesium content is the highest. The magnesium content of sample C is about four times that of A but the aqueous alkalinity of C and A are of the same order. The magnesium carbonate is usually present in limestone as dolomite and /or in the form of a solid solution of dolomite in calcite. If it is present entirely in the form of dolomite, then the reactivity of such a limestone will not be different from others containing lesser amounts of magnesium, since dolomites are known to be less reactive than limestones[1]. But magnesium carbonate present in the form of solid solution is likely to increase the reactivity of limestone because of the strain developed in the crystal stucture of calcite on account of substitution of Ca^{2+} by Mg^{2+}. The instability of limestone will increase with the increase of the amount of magnesium carbonate present in the form of a solid solution in calcite[9]. It appears that the high alkalinity of samples F and D may be due to the above causes. Magnesium carbonate present in C may be as dolomite, hence its lower reactivity. The use of limestone containing high magnesium content should be used only after checking its reactivity as there is likelihood of its being more reactive.

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Notes & News

New Ammonia Recovery Process

U. S. Steel Corpr. is constructing a large ammonia plant (1100 s. tons/day) at Clairton using a new process (U.S. Pat. No. 3,024,090; Brit. Pat. No. 958,054) to prepare coke oven gases for cryogenic processing and ammonia production. Overall ammonia recoveries using the new process are said to reach 99.5 per cent, and yields a cleaner gas for the cyrogenic phases of the operation. The process also avoids byproduct ammonium sulphate.

In this process, a 40 per cent solution of ammonium phosphate, having the molar ratio of ammonia to phosphoric acid less than 1.5, is recycled to absorb ammonia from the cooled coke oven gas. The enriched ammonium phosphate solution is then reboiled at atmospheric pressure or at 150 psig in a distillation tower that separates ammonia vapour and returns a lean phosphate solution for recycle.

Coke oven gas is collected in suction mains at about 700°F and cooled to 170°F in the transit. Tar and water in the gas condense out and the mains are continously flushed with sprays of recycled ammonia wash liquor. About 250 gals. of wash liquor is used for each ton of coal. From the suction mains the partly cooled and condensed gas passes to the primary coolers, where it is further cooled by counter-current cascade of water to 100°F, and thus condense out tar and coke oven benzene, toluene and xylene and about 15 per cent ammonia. The remaining 85 per cent ammonia passes on. Thus ammonia is recoverable both from the cooled gas leaving the top of the primary cooler and from the condensed ammonia liquor collected in the suction mains and the primary cooler bottoms.

[Nitrogen, No. 34, (1965), 37]

500,000 tons/yr. of Ammonia

In the last few years the trend to increase plant capacity of ammonia production has become very important, because of a greater demand for food. In recent years production of synthesis gas based on coal, which is dependent largely on the location, has become limited in scope due to gasification having to be effected under atmospheric pressure. As a result of greater exploitation of crude oil, refinery products and material gas and pipeline transport of these, large quantities of raw materials can be supplied cheaply to the traditional centres of industry. Besides, intensive automatic control of operations and the development of long-lasting equipment guarantee economic non-stop operation.

The economics of the design of larger units, viz. 300, 500, 1000 and more tons/day of ammonia is now being investigated. Investment costs are found to decrease, the number of staff is reduced proportionally as is the operating and maintenance personnel required for each line, independent of capacity. Energy expenditure and gas losses do not only decrease relatively but also absolutely as for instance, leak gases can be recirculated. The expenditure of energy is dependent largely on the choice of compressor units and the way these are driven. Accordingly, this part of the processing costs amounts to 30-40 per cent of the total cost of the ammonia synthesis unit.

Maintenance problems are of more importance and hence the constructive design detail of equipment items, since costly production loss increases rapidly with larger units under constant repair. This production loss can amount to approximately £2,000 per hour in a plant with a capacity of 1500 tons/day of ammonia. Accordingly, optimum production is that of about 1000 tons/day of ammonia.

There are limitations because of problems of transport, viz. transport of finished products and of the heaviest items of equipment. The heaviest load for transportation severally amounts to no more than about 100 tons per piece of equipment. The foundation for heavy load equipment is also likely to pose problems. Therefore a converter operating in the horizontal position will be preferred. This then leads the answer, viz. 1500 tons/day ammonia (equivalent to 500,000 tons/yr) in one line represents an adequate maximum. The author has given a sketch of the most favourable design for the synthesis loop.

With regard to the major item of equipment viz. ammonia converter, the condition for weight limit will be satisfied in its optimum value at an operating pressure of 200 atm. The recovery of the heat of reaction from the synthesis loop can be effected most economically by means of a high-pressure steam generator, with high pressure air or water coolers in series. In order to keep the weight limit of the converter, insertion of a more expensive low-temperature cooling system will be necessary for production of about 600 tons/day of ammonia at lower pressures.

For compression of large quantities of fresh gas to 200 atm. and for circulating the gas, turbo-compressors of the barrel-type are available.

[ibid, 32]

TVA's Fertilizer Technology Demonstration

The series of demonstrations, fifth of its kind, organized by the Tennesse Valley Authority under the aegis of its Division of Chemical Operations at Wilson Dam, Alabama, during Oct. 6-7, 1964 was attended amongst others by 80 representatives from 20 other countries. Immediately after the address of welcome and the brief reviews of recent TVA activities, the visitors were invited to take part in organized tours of the phosphate and nitrogen plants and also the pilot plant and research laboratories where advnaced fertilizer production techniques were demonstrated. It has made important progress in the direct production of concentrated wet-process phosphoric acid and polyphosphate derivatives as well as in the development of new high analysis solid and liquid fertilizers, and also various ways of incorporating micro-nutrients.

Phosphoric Acid: TVA demonstrated on a small scale that the process for making acid in the 50-55 per cent P_2O_5 range without the need for evaporation is now a near reality. Phosphate rock is reacted with fuming sulphuric acid in a pug mill and a rotary drum for 45 minutes producing a semi-granular acidulate and simultaneously evolving 75 per cent of the flourine present in the rock. The acidulate is then leached with counter-current hot water for about 1 hr in a tubular inclined rotary extractor fitted with an internal helix. Concentrated phosphoric acid (with 55 per cent P_2O_5) emerges from the lower end of the extractor and anhydrous calcium sulphate discharges from the upper end.

In the hemihydrate-foam method, a pilot-plant of which was demonstrated, ground phosphate rock is first pre-mixed with 30 per cent P_2O_5 phosphoric prior to reacting with concentrated sulphuric acid which is introduced via the foam present on the surface of the agitated slurry in the reactor. Phosphoric acid (with 40 per cent P_2O_5) together with calcium sulphate are produced, and the latter is filtered and washed. Extraction and washing efficiencies of about 94-96 per cent can be obtained. Further studies on sludge reduction are in hand. The major component of most of these sludges is a complex salt having the composition (Fe, Al)$_3$ KH_{14} $(P0_4)_8$ 4 H_2O and precipitation will continue until almost all of the potassium in the acid is removed.

The latest activities of TVA include the production of a furnace acid containing 83 per cent P_2O_5, which is almost non-corrosive to mild steel and does not crystallize on extended storage at ambient temperatures. It can also be ammoniated to yield a liquid of 11-40-0 grade that does not crystallize at 32°F, since ammoniation reduces the original non-ortho percentages from about 95 to 80 per cent and simultaneously increases solubility. The 83 per cent P_2O_5 acid offers useful savings in transportation costs.

Polyphosphates: A process, whereby ammonium phosphate of certain grades can be produced directly from wet process (or furnace) phosphoric acid, thereby avoiding the use of more costly superphosphoric acid, was demonstrated. In the pilot plant, 54 per cent P_2O_5 wet process acid is ammoniated counter-currently in a 2-stage system—the first stage at atmospheric pressure and the second at about 1 psig. Water is evaporated from both stages and the melt from the second reactor is granulated in a pugmill with recycled fines. A typical product is 12-58-0 of 6-12 mesh, which dissolves easily in water or aqueous ammonia to produce a variety of sequestered fertilizer solutions.

TVA's work include petrographic and x-ray studies to identify the many complexes formed. It has investigated several methods of production of potassium polyphosphates—mostly based on heating phosphoric acid with KCl in the range 600°-1500°F. Economic use of the free HCl will be made possible.

Nitrogen Fertilizers: By removing the condensed water in cyclones and distributing it to the absorber under optimum conditions, the strength of nitric acid has been increased to 62 per cent HNO_3, and another high-pressure plant capable of producing 67-70 per cent HNO_3 has gone on stream. These strong acids are intended to produce high analysis fertilizers based on ammonium nitrate and nitric phosphates in full scale units now under construction. The use of pan granulators with preneutralizers and reactor-evaporators enables granular products to be made from NH_3 and $HN0_3$ or mixture of strong acids according to the desired grades e.g.35-0-0, 30-10-0 or 18-18-18 if potash is added. Another development is an adaptation of the TVA ammoniator-granulator process to make high nitrogen grades, such as 25-35-0, 34-17-0 and 20-20-20, from phosphoric acid plus once-through or partial-recycle urea slurry and corresponding off-gases, leading to substantial savings in capital and operating costs.

Nitric Phosphates: Recent research work includes the use of a pre-neutralizer to reduce recycle requirements, the use of 65-70 per cent HNO_3 and superphosphoric acid, investigations to increase (i) the flexibility of the process, (ii) the P_2O_5 water solubility of the products, and the number of grades. A pilot plant demonstrated that 15-15-15 and 20-20-0 could be produced with recycle ratios of 3 or less, and products with P_2O_5 water solubilites between 40 and 60 per cent. These products were satisfactory when coated with 2 per cent kaolin clay or 1 per cent surfactant-treated clay.

Recent work has been undertaken on formamide ($HCONH_2$), a liquid with low vapour pressure containing 31 per cent nitrogen. According to green-house tests, it has an agronomical value as good as that of urea.

Liquid Fertilizers: 11-37-0 and 10-34-0, made by ammoniating furnace and wet-process super phosphoric acid respectively, are now in much use. These base solutions mix readily with urea-ammonium nitrate solutions and potash to yield a wide range of sequestered liquid fertilizers e.g. 19-19-0, 7-21-7, 17-17-0 and 5-10-10. When ortho-wet process acid is also used to make liquid fertilizer, polyphosphates in 11-37-0 or 10-34-0 base solutions will sequester impurities introduced by the ortho-acid.

Suspension fertilizers have also been under active investigation and a recent TVA investigation includes a range of such fertilizers made from phosphate rock, nitric acid and ammonia. Bench-scale work indicates that all of the P_2O_5 in the rock can be solubilized when HNO_3/rock CaO mole ratio is about 1.85, and ammoniation can be undertaken to a NH_3:NHO_3 mole ratio of about 1.0 provided about18 lb H_2SO_4 per ton of product are added.

Triple superphosphate has also been investigated as a substitute for phosphoric acid in suspension fertilizer. The two major factors of importance are: the sequence in which the ingredients are added and the degree of ammoniation undertaken. A typical suspension formulation is 10-10-10 made from TSP, aqua-ammonia-urea-ammonium nitrate solution, potash and water.

An unusual application of liquid ammonium phosphate fertilizers is the fighting of forest fires using 11-37-0 concentrates.

Micronutrients: Most micronutrients are much more soluble in 11-37-0 polyphosphate base solution than in 8-24-0 made from ortho-phosphoric acid. Improved methods of adding micronutrients to solid fertilizers are being developed. A method of coating granulated fertilizers with the desired micronutrients in finely divided form prior to bagging or bulk blending or to use oil or water as a binder holds out promise. The coating of soluble fertilizers with sulphur as a means of controlling nutrient release to the soil and as a possible method of incorporating micronutrients is under current investigation.

[C.J. Pratt, Brit, Chem. Engng, 10 (1965), 319-322]

High Pressure Steam Hydrocarbon Ammonia Synthesis

Developments in catalysts and in reformer furnace have permitted sizeable increase in the pressure level of catalytic reformers in more recent ammonia plants.

For high pressure reforming a suitable reformer pressure range is 350 to 450 psig, the actual level selected depends on price structure, plant capacity, compressor size and type, etc. The high reforming pressure no doubt reduces compressor gas reformer cost and increases unit thermal efficiency, but the unfavourable methane-steam equilibrium requires more steam or higher operating temperatures for a specific design. The higher pressure requires more horse power for feed and air compression equipment and major pumps, and extreme increment also raises operating pressure of down-stream equipment. There is no single optimum pressure applicable to all reforming systems, situations and hydrocarbon feeds. Orland J. Quartulli of M. W. Kellogg Co. has discussed some aspects of high pressure reforming (200-500 psig) that relate to performance and operating cost with particular emphasis on steam-carbon ratio, residual methane, hydrogen-nitrogen ratio, inert purge, heat recovery, power requirements, compressor selection, feed and utility price structure [Hydrocarbon Processing & Petr Refinr., 44 (1965), 4, 151]. The following 3 ammonia flowsheets having high pressure reforming systems are his basis: (1) catalytic steam-hydrocarbon reforming using single shift conversion and methanation for raw synthesis gas purification, (2) same reforming using double shift conversion, and (3) same using single shift conversion and copper liquor scrubbing for raw synthesis gas.

Flowsheet (1): It is a 2-step process consisting of primary and secondary conversion of hydrocarbons to a raw synthesis gas. In the primary step, steam and hydrocarbon are preheated and delivered to externally heated reforming tubes containing nickel reforming catalyst wherein hydrocarbon is partially converted to hydrogen and carbon oxides. In the secondary steps the partially reformed gas and process air are introduced into the secondary reformer, where partial combustion of the primary reformer effluent elevates the temperature of the mixed gas and supplies the energy required to complete the reforming of hydrocarbon to the desired level. Next, the synthesis gas is shifted and CO_2 in it is removed, the residual carbon oxides in the treated gas are then removed in a catalytic methanation step. The methane is purged in the synthesis loop which also removes any argon and helium—if it is present in the natural gas feed. The single shift methanation process is popular because of design simplicity and operating ease. This feed has the highest feed rate.

The double shift conversion process is almost the same as the above except that it requires another stage of CO shift conversion and CO_2 removal, which reduces the residual CO. In certain cases, two solvents for CO_2 removal are used.

Used widely in the past, copper liquor scrubbing has found very little application now. Besides low utility costs, a synthesis gas having low residual methane is produced which allows a high conversion of hydrogen to ammonia and a low purge of inerts in the loop. This process requires less feed. Among disadvantages are high equipment cost, careful attention for maintaining the ratio of cuprous to cupric ions and because of the complex oxidation-reduction reactions occurring in the CO absorption.

Naphtha Reforming for Synthesis Gas

Light distillate reforming plants operating at pressure and producing gas for ammonia synthesis came into operation in 1960. Since then the process has been developed for the production of lean gas and recently for town gas of 500-520 Btu/ft^3. This steam-naphtha reaction is capable of producing a wide range of possible product gases depending upon the conditions of operation of the reformer. Provided the light distillate is completely reformed to molecules containing only single atoms of carbon, the following limiting possibilities exist: either the whole of the carbon is reformed to give oxides of carbon together with hydrogen in the product gas, or else the reforming proceeds to the limit where no hydrogen is present in the product gas and the maximum amount of carbon is reformed to methane.

For hydrogen production, the overall reaction is ideally as: $CH_2.1+2.OH_2O \rightarrow CO_2+3.05H_2+49$ kcal. In practice, only about 99 per cent conversion to carbon oxide is attained.

For ammonia synthesis gas production, the necessary nitrogen content being introduced as air into the secondary reformer—a catalyst filled vessel in which the air is burnt liberating heat and raising the temperature of the product gases—and bringing a secondary reformer product gas equilibrium at 150°-200°C higher than that of the product gases from the primary reformer. The overall reaction taking place over both reformer is ideally as: $CH_2.1+1.54H_2O+1.1\ \text{Air} \xrightarrow[+17.7\ \text{kcal}]{} CO_2+0.86\ (N_2+3H_2)$.

For lean gas production, although the flow diagram is similar to that for hydrogen production, the operating conditions markedly differ. A typical stoichiometry for an ICI lean gas reforming plant is: $CH_2.1+1.30H_2O \xrightarrow[+31.5\ \text{kcal}]{} 0.1\ CO+0.6\ CO_2+1.75\ H_2+0.3\ CH_4$. Conversion to carbon oxides is only 70 per cent complete, so that a lean gas reformer operates at a markedly lower temperature than a hydrogen reformer.

For town gas production, ICI has recently developed a reforming process which eliminates the need for butane enrichment. Its overall stoichiometry is as follows: $CH_2+0.85H_20 \xrightarrow[16.9\ \text{kcal}]{} 0.05\ CO+0.40\ CO_2+0.80\ H_2+0.55\ CH_4$. Conversion of the light distillates to carbon oxides is now only 45 per cent complete and the required equilibrium reforming temperature is even lower than for lean gas production.

A typical ICI reforming furnace is of rectangular construction lined with refractory brick-work on all sides and the reacting gases pass downwards through catalyst filled tubes of about 4 in. bore and 30 ft. heated length, suspended in rows in the furnace. Oil burner fire downwards from the roof into lanes between the tube rows and the flue gases are removed through ducts built up on the floor of the furnace.

The reformer equilibrium temperatures generally lie in the range 650°C for town gas production to over 1,000°C for ammonia synthesis gas production. Since the tube wall temperature must exceed the reformed gas temperature by some 100°C to permit reasonably rapid heat transfer, it is evident that tube wall temperature must lie at about 750°C upwards, at which the tube metal creeps under stress.

When designing a top fired reformer, detailed consideration must be given to the distribution and magnitude of the heat fluxes and gas temperatures in the furnace and in the tubes in order that the tube wall temperature can be calculated accurately.

The reformers for ammonia synthesis gas production are not limited in operating pressure by metallurgical considerations as much as are hydrogen producing re-

formers. The final reforming is effected in the adiabatic secondary reformer after the addition of the necessary nitrogen, For lean gas and town gas manufacture, the reforming equilibrium temperatures required are markedly lower than for hydrogen production or ammonia synthesis gas production. Pressures about 35 atm. pose no severe metallurgical difficulties.

The present ICI reforming catalyst is capable of reforming completely feedstocks from straight-run liquid petroleum distillate fractions with final boiling points upto 220°C and, suitably modified, can process other refinery streams in this boiling range.

[S.P.S. Andrews, Chem. & Indus., No. 20, (1965), 826-830]

Nitrogen Fertilizers World Wide

World consumption of fertilizer nutrients, viz., nitrogen, phosphate and potash, has grown from about 3 million tons at the end of first decade of this century to over 30 millions currently. During the last decade fertilizer consumption has doubled. An interesting feature of this increase is that the major centres of consumption are tending gradually away from the industrial regions towards the primary producing and developing regions. A second feature is that production is still concentrated to an appreciable extent in the industrial regions viz. western Europe, N. America and Japan. Of course now the centres of ammonia production are beginning to move towards the new centres of consumption. World trade in fertilizer nitrogen has grown from one million in 1950 to nearly 3.5 million metric tons, or a quarter of world consumption.

In recent years tremendous strides have been made in reducing the cost of ammonia production both by increasing the size of plants and by introducing new processes. The economic significance of these developments may be seen from Table 1. The steam reformation process using either naphtha or natural gas has a distinct economic advantage over partial oxidation process.

TABLE 1—ESTIMATED COSTS OF AMMONIA WORKS

	Plant Capacity	
	66,000 *S.tons/ yr.*	230,000 *S.tons/ yr.*
	Works Cost, $/ton	
	$	$
Partial Oxidation Process		
Coal at $ 6.50/ton	45.0	39.5
Fuel Oil at $ 0.06/ gal.	43.0	38.0
Naphtha at $ 0.008/ lb.	41.5	36.0
Steam Reforming Process		
Naphtha at $ 0.008/lb	38.5	33.0
Natural Gas at $ 0.40/MCF	34.0	28.5
Natural Gas at $ 0.20/MCF	27.75	22.5

TABLE 2—PROCESS COST COMPARISON

Capacity, (s. tons/yr.)	66,000	230,000
	Battery limits Plant investment, $ million	
Partial Oxidation Process		
Coal ..	8.4	
Fuel Oil ..	6.6	
Naphtha ..	6.4	
Natural Gas ..	5.6	
Steam Reforming Process		
Naphtha ..	4.7	11.9
Natural Gas ..	4.0	10.4

While substantial reductions have been made in the capital costs of new ammonia plants, the new processes have also achieved marked reductions in raw material costs and improved energy utilization efficiency. As a result, fixed (or indirect) costs still account for an appreciable amount of the total work costs (say 30-40 per cent). Where variable costs (direct costs) are substantially lower than total costs there will continue to be a strong economic incentive with new large plants to run them at near capacity.

The indigenous capital available for expenditure on imports is considerably lower in the developing countries than the industrial countries. The oil-producing developing countries are an important exception to this. Table 2 shows the approximate capital expenditure for a relatively small and large ammonia plant based on various processes and raw materials. In the developing countries between 25-50 per cent of the total capital cost of investment depending on local circumstances would need to be imported.

[O.T.W. Price, Chem. Engng. Prog., 61 (1965), 4, 20]

Fertilizer and Famine

The populations in Asia, Africa and Latin America are growing at rates of 2.3, 2.4 and 3.0 per cent per year respectively, which are the highest growth rates in history and are frequently referred to a 'population explosion'. But at the same time the production of food in these continents (total population in 1960 was 1,373 millions) has remained constant for the last 4 years—per capita productions of grain per day have declined from 16 and 21 to 15 and 18 ounces in Asia and Latin America whereas in Africa it has remained 150 ounces per day for the last 7 years. There is no social or economic development in these continents, that seems likely to increase food production enough to feed 900 million more people in 1980. According to Professor Raymond Ewell,* of State University of New York, if this trend continues for a few more years, a famine on a scale never experienced before in the world's history will inevitably result in the near future (1970-1980). For averting such a disaster, the professor offers the following solution: (i) reduction of population growth and (ii) increase of agricultural production or both.

Of the various technical factors, increased use of fertilizers offers the best possibility for a quick increase in agricultural production. From FAO Freedom from Hunger Campaign, the following increased yields: In Turkey 120 kg. plant nutrient per hectare on corn has given 85 per cent increase in yield; in Lebanon 52 kg/hectare on wheat has given 101 per cent increase; in Ghana 44 kg has given 52 per cent increase in rice and in Ecuador 45 kg has given 71 per cent increase in the yield of potatoes. These increases have been obtained by locally available seed

* Address at a meeting of Division of Fertilizer and Soil Chemistry, American Chemical Society, Illinois, Chicago, Sept. 1, 1964.

varieties. With improved seed varieties combined with increased quantities of fertilizer, much greater increases could be obtained.

For the 400 million additional population, in 1970, would require 15 million tons of nutrients in all three continents compared to 3 million tons in 1960-61 and about 4 million tons in 1963-64. For feeding 900 million additional population in 1980, 30 million tons of nutrients would be required. These figures have been calculated on the following basis: (i) 8 tons of grain yield per ton of plant nutrient and (ii) two-thirds of fertilizer would be used on grain, one-third on all other crops.

TABLE—Agricultural Output of Different Countries

	Number of People/100 Acres of Agricultural Land	*Number Engaged in Agricultural Occupation/100 Acres of Agricultrual Land*	*Value of Food Production/Person Engaged in Agriculture, £/Annum*
Northern Europe	88	5.8	575
India	100	28.9	33
Japan	527	101.0	66
U.S.A.	16	0.5	1896
Australia & Newzealand	1	0.1	1786
W. Central Africa	17	5.0	51

Food Situation in Developing Countries

In the western countries less than 15 per cent of the working population produces food in great abundance, while in the rest of the world more than 30 per cent of the working population are engaged in producing food, whose output is inadequate. Increase in agricultural output comes from two sources viz. cultivating more land and improving the productivity of land already in cultivation. For example, the enclosure movement in Britain opened the way for using land more efficiently followed by movements like Norfolk fourcourse rotation and the system of wintering stock in fold yards. In our time, the fertilizer revolution has enabled us to improve as well as conserve, and raise soil fertility to undreamt of levels.

European farming advanced from shifting to continuous cultivation at a low level of fertility in the Middle Ages, very similar to the agriculture now practised in India. The transition from this exploitive to progressive agriculture begins when farmers recognize the value of crop wastes, animal and human excreta, and certain wastes of human community life, and organize their distribution for increasing crop yield.

The fertilizer industry, whose development began first in the industrialized regions of western Europe, released agriculture from the need to take nutrients from one field to improve another. Nevertheless, the lands most closely associated with urban areas have profited most.

A factor seriously restricting artificial fertilizers spreading to the low productivity areas is that land at poverty level, either through long continued exploitive farming or as a consequence of weathering and leaching for many million years, is often so poor that it hardly responds to simple fertilizer treatments. Moreover, the interaction of fertilizers and water supply is more critical in the tropics than in the mild and more reliable climates of the north temperate regions. In contrast, the already fertile lands of western Europe respond readily to the application of fertilizers, and in general no nutrient element is in very short supply. Nitrogen, which is usually furthest below the optimum, alone increases yield considerably. In the tropics, response to fertilizers may be nil, or even negative, in years of inadequate rain. Alternatively, low soil permeability, with consequent run-off in the rains and early drought when the rain cease, may make the available water ineffective. In addition to this uncertainty, the limited resources of the cultivators further restrict output.

In Japan, the increase in the yield of rice has been brought about by controlling water on the land ensuring no erosion losses and using the silt, maintaining fertility in this way and using the night soil and compost for a long time for producing soil conditions which benefit by fertilizer application.

In the tropics, fertilizers were used first in plantations, but the fertilizer revolution has hardly touched the areas with very poor soils with little part in modern money economy. The research by Lawes on the improvement of cotton yields in northern Nigeria—by early sowing, using improved varieties and applying phosphates—indicated a maximum potential yield of about 600 lb/acre. After improving the soil moisture status, applying fertilizers, like nitrogen and phosphate, became more profitable. The cumulative effect of all these measures resulted in an yield of 2000 lb/acre on his high fertility plots, which is an example of the need to remove all the limitations on production at once to achieve a real improvement. Recently in Uganda, the application of organic manure together with a fertilizer mixture containing nitrogen, phosphates, sulphur and calcium has broken a long history of nil responses to fertilizer dressings. In many parts of the developing countries, techniques for improving fertility by applying fertilizers have already been worked out for favourable conditions of soil and cropping systems and fertilizers have become part of standard agricultural practice. On the more unresponsive soils the technical problems of improving fertility are still formidable, and enormous economic obstacles still stand in the way of establishing a rising standard of soil fertility.

[J. B. Hutchinson, FRS, Discovery, 26 (1965), 5, 20]

Rumania's Nitrogenous Industry

Recent developments in Rumania have been characterized by the priority expansion of chemical industry following the post-war period of reconstruction and plant rehabilitation. It is only within the last decade that a progressive expansion of fertilizer industry has taken place. In addition to the increased availability of investment resources, the production of nitrogenous fertilizers has been benefited from the indigenous deposits of natural

gas and oil located throughout the country.

Rumania ranks fourth in the world and second in Europe in the size of her natural gas deposits. The methane content of the natural gas is about 99 per cent, while the same in the casing-head gas is 64-90 per cent. The reserves of natural gas are estimated to be 575,000 million cubic metres and those of crudes oil are of the order of 150 million tonnes. Between 1960 and 1963, output of nitrogenous fertilizers increased more than fourfold to a level of 84,850 tonnes of N in 1963, while phosphate fertilizer production rose by only 91.5 per cent during this period to just under 100,000 te P_2O_5 in 1963. If the current plans are adhered to, a further trebling of nitrogen production will be implemented by 1965. By this time it is estimated that Rumania will be in a position to supply her agriculture with approximately 2 million tonnes of fertilizers, equivalent to 200 Kg./hectare of arable land, which contrasts markedly with 1960 level of consumption of only 8 kg./hectare.

At the end of 1963, the plant capacity for nitrogen fertilizer amount to around 134,000 te N. It has been produced since 1936 when a 1800 t.p.a. ammonia plant was brought on stream at Tarnaveni, based on natural gas from the Translyvania plateau. Immediately after the Second World War, a major reconstruction programme was initiated to restore damaged chemical plants and new facilities were also installed. Included among these was the chemical combine at Victoria, construction of which had been started by the Germans, in 1940. This nitrogen plant, using natural gas, was completed in 1949 by Russian assistance, its present capacity being 15000 of N as ammonium nitrate. A synthetic ammonia plant was also built at Fagaras, on the periphery of the Transylvania gas-fields, but this was destroyed during the war. It has since been rebuilt and enlarged to an annual capacity of 33,000 tonnes N of ammonium nitrate.

Production at the above plants has been supplemented by the start-up of operations at the Piatra Neamt nitrogen fertilizer work built with Soviet Union's assistance. It was brought into full production recently with an annual capacity of 210,000 tonnes of urea and comprises part of a large chemical complex at Savinesti. It incorporates up-to-date process such as the oxidative conversion of methane gas and gas-washing in the production of ammonia and the absorption under pressure of nitrogen oxide in water in the production of nitric acid. It is planned to double ammonia capacity at Piatra Neamt in the near future and a large urea facility will be installed; urea will be used both as a direct-application fertilizer and as an intermediate for the production of complex fertilizers. A large complex fertilizer plant is to be erected on site, and further units will be added to produce ammonia liquor for use as a fertilizer material. In addition to these plants, nitrogen fertilizers are also produced in the form of ammonium sulphate recovered from steelworks at Hunedoara and Resita at the rate of approximately 15,000 t.p.a.

Three new projects are at present under construction for intensifying chemical fertilozer production. The largest undertaking is the chemical combine at Craiova, in south-west adjacent to Arges-Oltenia gas-fields, which is scheduled to produce 300,000 te of granulated ammonium nitrate and 100,000 te of urea using Stamicarbon process with equipment supplied by Fredrich Uhde of Germany. A 35,000 tpa acetylene plant will supply synthesis gas to ammonia unit.

Tirgu Mures, in the heart of the Transylvanian plateau, is the site of a second new nitrogen plant, which will have an ultimate capacity of 80,000 tap N.

Certain sections of chemical fertilizer complex at Turnu Magurele on the Rumanian/Bulgarian border have recently started operations following trial production period earlier in 1964. It will produce 400,000 tpa of granular compound fertilizers, based on the two-stage processing of natural gas, and 300,000 tpa sulphuric acid. The raw materials include pyrites from Moldova Nova deposits and apatite from N. Vietnam. Potash is imported from. E. Germany. A 200,000 tpa urea plant, based on Stamicarbon process, will be built by Fredrich Uhde in the near future.

The intense growth-rate planned for Rumania will reflect favourably on her contribution to total E. European capacity.

[Nitrogen, N. 33, (1965), 19-21]

Japanese Developments in Ammonia Synthesis

Japan Consulting Institute began developing a new ammonium synthetic equipment in 1959 and got its process patented in 1962 (Patent No. 296,343). In 1963, The Research Development of Japan, a Government body, entrusted the Nissan Chemical Co.Ltd. with the task of commercialising the above patent, and as a result a 50 t/d plant was constructed.

In this process, the reaction heat of synthesis of ammonia is recovered for producing high temperature steam. H_2 and N_2 gases in the ratio 3:1 compressed to 300-350 atm are fed into a condensing column along with the gas coming out of the circulating pump. This gas containing 7-8 per cent of NH_3 is cooled down to about -20°C after being passed through the condensing column and evaporator to liquefy and separate NH_3. Gas from the condensing column, which enters the synthesis tower, contains about 2 per cent ammonia. In the synthesis tower, reaction takes place at about 500°C. It is considered advantageous to raise the equilibrium of the NH_3 percentage by removing the reaction heat and for this the following extra equipments are incorporated: adiabatic catalyst layer, parallel cooling catalyst layer, high pressure circulation water cooler and lower heat exchanger.

The inlet gas exchanges heat with the reaction gas and removes the reaction heat as it goes down, in the tube for the parallel cooling catalyst and into the adiabatic layer via the central tube after it has reached 420°C. On account of the cooling by gas, the catalyst in the parallel cooling catalyst tube attains an optimum temperature distribution. The reacted gas enters the cooler at 480°C and then goes into a heat exchanger. By regulating the high pressure circulation water-cooler, the temperature distribution in the synthesis equipment is easily controlled.

Some of the features of the JCI technique are the following: (1) Since the temperature of the catalyst may assume the optimum temperature distribution in which the fluctuation in temperature is slight, the production of ammonia per unit capacity of tower is large; (2) there being no cooling coil in the catalyst layer, the equipment is subject to less failures and enables easy replacement; (3) as high-temperature, high-pressure steam is produced, the production cost of ammonia is fairly reduced; (4) life of catalyst is 3-5 years and the upper part of the adiabatic can be easily replaced when it deteriorates.

[Look Japan, 10 (1965), 110, 2-3]

Urea-Potassium Phosphate Complex Fertilizers

Among the chloride-free potassium-containing fertilizers, potassium metaphos-

phate is high concentrated containing almost 100 per cent nutrients—about 60 per cent K_2O and 40 per cent P_2O_5. For producing complex fertilizers containing the 3 basic nutrients, either mechanical mixing of the components at ordinary temperatures or decomposition of phosphates with nitric or sulphuric acid followed by introduction of ammonia and a potassium salt addition is the technique. However, in the mixing technique although products with a desired proportion of nutrient elements are easily obtained it is not always possible to achieve good physical properties or homogeneity, while the acid decomposition method yields good homogeneous products.

S. I. Volfkovich and V. S. Kalach [Internat. Chem. Engng., 5(1965), 2, 237-239] have mixed urea with potasssium phosphates and heated over a sand bath, when urea begins to melt (at 132.7°C) and then the solution of monopotassium phosphate (m. p. 252.6°C) is formed. About 40 parts of monopotassium phosphate are dissolved in 100 parts of urea. They studied the phase transformations at atmospheric pressure. The cooled mixture is a white, hard, well granulated mass and does not cake. It is free-flowing and completely soluble in water. Its hygroscopicity is 6.6 in Pestor scale. Micro amounts of fertilizers, like compounds of B, Cu, Mn, Mo, etc., can easily be introduced without impairing the physico-chemical properties of the complexes. Similar investigations were carried out on the mixing of urea with potassium metaphosphate.

The above investigations indicate the following: (1) high quality, concentrated fertilizers, containing 60 to 81 per cent nutrient elements, based on N, P_2O_5 and K_2O, and having good physical properties can be obtained by mixing urea with monopotassium phosphate or with potassium metaphosphate; (2) mixing urea, highly soluble potassium orthophosphate and potassium metaphosphate—which is slightly soluble in water—together with the introduction of micro elements makes feasible the production of complex fertilizers.

New Ammonia Process Using Naphtha

Society Chimique Grande Paroisse has developed a high pressure (450-500 psig) catalytic steam-reforming process using straight run 300°F naphtha resulting in amazingly low power requirements without increased consumption of raw material and fuel. It is also applicable to natural gas. A typical 500 tons/day ammonia plant has been described by J. P. Gignier and J. H. Quibel [Hydrocarbon Proc. & Petr. Refiner, 44 (1965), 3, 153-156].

A newly developed nickel catalyst, well suited for high pressure reforming (300-1000 psi), highly refractory and resistant to thermal shock and crushing has been used. Sulphur of naphtha is absorbed on zinc oxide by getting it converted to H_2S through a catalytic hydrogenation step. Naphtha vapours mixed with steam at a steam-to-carbon ratio around 3 for 500 psig reformer operating pressure are preheated to about 1000°F and distributed into the reforming tubes. The reforming furnace is made of two radiation cells, each containing one row of tubes heated from both sides. Air for the secondary reforming is compressed in one turbine driven centrifugal machine, then preheated before mixing up with gas from primary reformer at inlet of the secondary reforming reactor, which is a refractory lined low chrome steel vessel filled with nickel catalyst. This catalyst must show good activity in order to decrease the residual methane to 0.2-0.3 per cent and at the same time withstand 1800°F produced by the reaction.

The Co-conversion is performed first in two stages on standard iron catalyst. The steam ratios are not high enough to satisfy $CO+H_2O \rightleftharpoons CO_2+H_2$ reaction equilibrium at the very low residual CO which is desired. After the two stages of the so-called high temperature shift, the gas is further cooled by water injection and enters the low temperature shift catalyst bed where CO content is reduced to 0.2-0.4 per cent.

With activated potassium carbonate, such as the carbonate arsenite process, CO_2 can be removed down to 0.1 per cent and the steam content of the incoming gas is enough to supply the heat necessary for stripping the CO_2.

A conventional methanation step follows transforming the residual CO and CO_2 into methane which acts as an inert in ammonia synthesis. The gas is then cooled and is ready from 420-450 psig up to the synthesis pressure.

The main power requirements are given in Table 1. Three stage compression of the synthesis gas to 5000 psig is done by two 55 per cent reciprocating compressors, which also carry at the same time the gas circulation and the refrigeration services of the synthesis loop.

TABLE 1—POWER CONSUMPTION

Power Requirements Consumer	*Kwh/hr*
Air compressor	3,900
Synthetic gas compressors and circulation compressors, Refrigeration	11,700
Pumps, Fans, Miscellaneous	1,200
Sub total	16,800
Recovery	11,800
Net Consumption	5,000

The overall set up includes expansion of all the steam available in turbines driving an electric generator. Steam is produced in several spots of the gas generation and ammonia synthesis at the highest feasible pressures (1300 psig), then superheated and expanded twice, first down to the reforming process pressure, then for the excess steam in a condensing stage, producing the power recovery (see Table 1). This system incorporates all that is necessary for making the process self-supporting with additional fuel burning since a little more steam production and superheat would bring to the expanders all the energy necessary to fill the power gap.

The 5000 psig ammonia loop comprises besides the synthesis reactor the following equipment: waste heat boiler, boiler feed water preheater, gas-gas exchanger, air-cooled (or water cooled) condenser and separator, circulation compressor cold exchanger, and refrigerated condenser and separator. Fresh gas is introduced just ahead of the cold condensation which eliminates traces of humidity and oil from damaging the catalyst.

Integrated Fertilizer Production

Once the conception of integration is practised, it frequently leads to larger plants. In some cases, cost reduction advantages have been so great that they have blinded planners to possible difficulties. There are cases which involve the integration of functions of several units, which must be approached on the basis of an individual case and may be best done when the chemical engineering architectural plan is performed by a single organization. Functional integration of units processing gases and liquids thus leads to savings in production costs and invest-

ments, but achieving this requires an overall design concept and follow-through. It may also require plot area integration.

The first step in the design of the system is the determination of the area's needs. What crops should be grown and in what quantities? What soil treatment is required? What yields can be expected and how will these be affected by type and quantity of fertilizers? When should different types of fertilizers be applied to different crops for the best results? Another set of data needs to be assembled includes raw materials alongwith their costs and availabilities, plant site data, costs of utilities, cost of installation, etc.

The application of the above principles was used by Kellogg International Corpr. in S. America. Taking into consideration all the factors, they studied two granulating products as basic material, viz. a 30-15-0 and 19-9-0 products. The 30-15-0 would be produced by granulating the product of the reaction of nitric and sulphuric acids and ammonia, then reacting further with ammonia to the desired degree in the granulator. For 19-9-0, highly-acid superphosphate would be produced in the granulator, the excess acid in the superphosphate would be neutralized by ammonia.

The production of the required fertilizer would take place in a complex that included an ammonia, a nitric acid, an ammonium nitrate, a sulphuric acid and a granulation plants. To these would be added a phosphoric acid or a superphosphate plant. Two general concepts for the complex was followed viz. in one all plants to be located at one site with all raw materials transported to it, in the other the ammonia plant to be located where natural gas was available and ammonia shipped by truck to the site of the rest of the plants, which would be so located that transportation costs of phosphate rock and sulphur and of the finished products were minimised. Four locations for the complexes were considered and analysed.

[Chem. Age, 92 (1965), 2396, 923-924]

Prices of Fertilizers

With effect from Aug. 8, 1965, the Government of India has fixed the following Pool issue prices (per metric ton) of ammonium sulphate nitrate, urea and calcium ammonium nitrate in respect of their sales to distributors for consumption in tea, coffee and rubber plantations in the states of Kerala, Madras, Mysore, Assam and W. Bengal: ASN Rs. 412.00, Urea Rs. 585.00 and CAN Rs. 312.00.

The maximum price per metric tonne of the above fertilizers has also been fixed from the same date as given below (Table 1).

Indian Standards

1. Ammonium Chloride—A revised version of Indian standard specification for ammonium chloride, technical and pure, which was first published in 1957, has been brought by ISI. The revised standard, IS: 1113-1965, which prescribes the requirements and the methods of test of this product intended for use in soda ash industry, fermentation, soldering etc., incorporates changes made in the light of comments received after the publication of the original version.

2. Raw Bone Meal—The revised version, IS: 853-1964, prescribes the requirements for raw bone-meal used as a fertilizer. Provision has been made for prescribing limits of acid-insoluble matter, and the requirements for nitrogen content has been made applicable for water-insoluble portion.

TABLE 1—SCHEDULE OF MAXIMUM PRICE OF FERTILIZERS, Rs.

Fertilizer	*When Sold for the Use of Tea, Coffee or Rubber Plantations in Kerala, Madras, Mysore, Assam & W. Bengal*	*When Sold for the Use of Cultivators*			
		In U.P.	*In Madras*	*In Orissa*	*In any other State or Union Territory*
1	2	3	4	5	6
Ammonium Sulphate	374.60	366.00	370.20	373.00	360.00
Amm. Sulphate Nitrate	435.00	438.00	447.39	443.00	435.00
Urea	615.00	615.00	632.55	615.00	615.00
Cal. Amm. Nitrate	342.00	344.00	351.60	353.00	342.00

The maximum prices specified above except those specified in Col. 4 shall not include sales tax or other local taxes, wherever levied, while those specified in Col. 4 shall include sales tax.

News in Brief

Algae for Assessing Soil Fertility

A simple biological method using algal growth has been developed in Nottingham University for determining whether a soil is deficient in nitrogen, phosphorus and potassium. Special test papers, impregnated with different combinations of nutrient salts, are seeded with algal cells and incubated in contact with most soil under a light source for 6 days. The test papers have four distinct zones—zone A containing nitrogen, phosphorus and potassium salts in amounts needed for healthy plant growth. From each of the other zones one nutrient is absent, and therefore algal growth on these zones depends on the ability of the soil to provide the missing nutrients. At the end of the test period, the paper is dried, and comparison of depth of green colour in different zones indicates the extent of soil sample is lacking in nitrogen, phosphorus and potassium.

[New Scientist, 24(1964), 515]

Controlled Release of Trace Elements & Fertilizer

A new technique involving controlled release of trace elements and fertilizers containing requirements for healthy plant growth has been adopted by Cornish Manures Ltd., Norfolk, England. The trace elements, viz. magnesium, manganese, copper iron, zinc, molybdenum, boron and selenium, are as important to plant life as nitrogen, phosphorus and potassium, but which are absent in many modern fertilizers. Trials have shown an increase of about 1.5 per cent in the sugar content of sugar beet, an improvement in butter fat and total solids in the milk of a dairy herd, and a reduction in disease in apple, pear and plum orchards.

[Res. & Indus., 10 (1965), 143]

Fertilizers from Natural Gas in Holland

Staatsmijnen in Limberg has brought into operation a gas-reforming plant and has another nearing completion. It has a 40 per cent share in the partnership, known as Maatschap, for which gas is produced from the Groningen resources by N. V. Nederlandse Aardolie Mij (N.A.M.) who have the remaining 60 per cent holding.

Geleen is linked by a 24 in. pipeline with the main 36 in. pipe network that is being built to carry natural gas from Groningen in the north to various parts of Netherlands. The Geleen complex includes two plants built by Power Gas Corporation to produce ammonia synthesis gas by the ICI/Vetrocope process each with a capacity to produce the equivalent of 365 tons/day of ammonia.

[Brit. Chem. Engng., 10 (1965), 313]

Spray Dryer for Phosphate Fertilizer

American Agricultural Chem. Co. have installed a completely automated, 26 in. diameter, stainless and carbon steel Bower spray-dryer for drying a solution of two phosphates to economically produce a very homogeneous mixture. Feed solution is sprayed into the dryer by spinning atomizer wheel on the Bowen Spray Machine. Gentle but instantaneous drying prevents separation of two orthophosphates. The material has a moisture content below 0.3 per cent and is conveyed directly to the calciner. Fines are scrubbed in a wet scrubber and recycled.

[Phosphorus & Potassium, No. 15, (1965), 44]

Complex Phosphate Fertilizer

Laboratory investigations in Rumania have established the conditions required to obtain a 15-30-15 complex fertilizer based on ammonium phosphate. These consisted of ammoniation of 38 per cent P_2O_5 phosphoric acid produced by treating Vietnamese phosphorite with sulphuric acid and correction of the N: P_2O_5 ratio with 60-80 per cent urea solution, addition and return granulation, KCl (K_2O 60 per cent). Drying of granules by fluidization required a minimum drying time with nitrogen losses below 1 per cent.

[Phosphorus & Potassium, No. 16, (1965), 37]

Phosphate Concentration Plant in UAR

Rumania and UAR recently concluded an agreement for building a phosphate beneficiation plant with an annual capacity of 600,000 tonnes near Kosseir on Red Sea. Rumania will assist in expanding phosphate rock production in this area to a level of million tpa., and will also engineer and supply the equipment for both these projects. Rumania Mining Research Institute has been responsible for developing the technology for beneficiating the phosphate rock. The basic operations involved will be a washing stage to remove clay formation, followed by calcination combined with further washing to remove calcium and magnesium carbonates. The final product should contain 33-35 per cent P_2O_5.

[Phosphorus & Potassium, No. 16, (1965), 3]

Iron-Nitrogen Fertilizers from Waste Picklings

Iron-nitrogen fertilizers have been obtained in the USSR by treating pickling solutions with ammonia and ammonia liquor. These fertilizers contain in addition to iron hydroxide, up to 300 g./l. ammonium sulphate and in certain instances ammonium nitrate and "ammophos". Production of such liquid Fe-N fertilizers is simple and can be effected at any metallurgical plant.

The waste pickling solution (containing ferrous sulphate) can serve as an effective absorbing agent for removing nitrogen oxides from industrial gases. The pure nitric oxide thin regenerated can be used for direct synthesis of nitric acid. After evolution of nitric oxide the solution is

treated with ammonia and a liquid Fe-N fertilizer is obtained.

[Nitrogen, No. 33, (1965), 37]

Fertilizer Production in Poland

The output of nitrogenous fertilizers, which totalled 360,000 tonnes N in 1964 is expected to increase to 1,180,000 tonnes N by 1970 as a result of introduction of vast new production capacity in Pulawy and Plock and to the expansion of existing plants at Chorzow, Tarnow and Kedzierzyn. Long-term plans anticipate a total output of 1.7 million tonnes N by 1980. The following will be the range of products in 1970: ammonium nitrate and urea will account for 72 per cent of the total output, while nitrogen-based complex fertilizers are expected to account for over 8 per cent. Calcium cynamide, nitrochalk and calcium nitrate supply only 8 per cent of total nitrogen production. Consumption per hectare of arable land will increase from the present 24 to 77.4 kg. by 1970.

[Nitrogen, No. 33, (1965), 6]

Biological Production of Fertilizers

For a number of years the Agricultural Research Council of UK has supported research on the biological fixation of nitrogen, and studies on biological fixation by micro-organisms of atmospheric nitrogen have been carried out at the Imperial College, London. Workers there have succeeded in obtaining consistently active cell free extracts of *Azotobacter*. They are now hoping to elucidate the mechanisms of enzyme action by means of isotope technique which has proved fruitful with *Urease*.

[Nitrogen, No. 33, (1965), 35]

Ammonia for Preventing Corrosion

Work carried out jointly by the Central Electricity Generating Board and British Petroleum Co. Ltd., has indicated that corrosion of the primary air-heater tubes, caused by acid condensation, could be reduced to the extent of 73 per cent with ammonia injection. Examination of tube wastage before and after some 3000 hours of boiler operation with each additive shows that the estimated life obtainable with ammonia injection would be 12 to 16 years.

[Nitrogen, No. 33, (1965), 36]

New BASF Process for Synthesis Gas

At the Ludwigschafen works, a massive plant is working for some time, which produces synthesis gas from petroleum fractions by a catalytic process. This autothermal process will play a prominent part in Badische's conversion to petroleum feedstocks. It is said to match ICI's steam-reforming process in yield and economics, but whereas ICI uses pipe furnaces BASF employs converters of 3 metre diameter in which the catalyst is arranged in several successive layers.

[Chemische Industrie Internat., June (1965), 64]

NPK Fertilizer with 11 Trace Elements

Cornish Manures Ltd., of Kings Lyun, Norfolk (U. K.), are marketing high analysis granular NPK fertilizers containing 11 trace elements in slow release form. The gradual release of these elements is controlled by soil moisture, and it is claimed that this method has the advantage that the elements are available during the whole cropping period but are never present in sufficient concentration to induce toxicity, nor are they leached out quickly. It is claimed that these compounds provide the requirements of normal cropping. The slow-release elements are at present incorporated in 5-10-20, 6-15-15 and 10-10-18 compounds.

[Internat. Fert. Correspondent, June 1965; Abstr., FCI Ltd. P&D Abstracts, 3 (1965), 7, 1]

Sphero-form—A New Fertilizer Process

CEPCO Inc. Norfold, Virginia have announced a new process, similar to Dorr's ammophos process, of fertilizer manufacture called Sphero-Form. This process is an outgrowth of studies on thin film and surface forces on fine particles. It converts an essentially solid feed into granules under the conditions of ammoniation, but with less ammoniation loss than similar processes. CEPCO claims increased product quality is due to seeding at the ammoniator-granulator under conditions confining pellet growth to acquisitions of this coats. These are easily dried and the unusally uniform product size and roundness.

[Commer. Fertl. & Plant Food Indus., 110 (1965), 5, 47-45]

Bulk Blending of Fertilizers

The materials most commonly used for bulk blending are ammonium nitrate, ammonium sulphate, triple superphosphate, diammonium phosphate (18-46-0 or 16-48-0) and potassium chloride. Less commonly used materials include urea, ammonium phosphate nitrate (30-10-0), monoammonium phosphate (11-48-0), ammonium phosphate sulphate (16-20-0) and ordinary superphosphate. Some manufacturers offer a series of ammonium phosphate nitrates.

Bulk blending works best with well granulated, closely sized and sufficiently dry and strong materials. Ammonium phosphates are favourite blending materials.

Intimate blending is most important in preparation of bulk fertilizer materials. TVA has studied mixers—rotary drum type and tower blenders.

[(Agri. Chem., 20 (1965), 5, 21-22)]

Coal-Based Fertilizer

A lower-price fertilizer containing 22 per cent N has been developed by the Alberta Research Council, Canada, to compete with ammonium sulphate. The process comprises combining powdered sub-bituminous coal, found in large quantities on the prairies, with air and ammonia at 570°F. The material, as claimed by Dr. Berkowitz, is specially suitable for humus-deficient soils.

[ECN, 8 (1965), 180, 4]

Fixation of Nitrogen in Plasma

At the 20th International Congress of Pure and Applied Chemistry held in Moscow in July 1965, Prof. Sheindlin, Corresponding Member of the U.S.S.R. Academy of Sciences, announced that Soviet scientists had developed a method of fixation of atmospheric nitrogen in a plasma stream. This process is expected to revolutionize the fertilizer industry.

[Science News, July 16, 1965, p. 2, U.S.S.R. Embassy in India]

Miscellaneous

Sarbasri M. Samaddar, M.Sc., and Ranjit Kumar Choudhuri, M.Sc., both Research Physicists (Geology), have been elected Fellows of the Geological, Mining and Metallurgical Society of India.

STATISTICS

TABLE 1—APPROXIMATE REMOVAL PER HECTARE, OF NITROGEN, PHOSPHORUS AND POTASSIUM BY SELECTED CROPS (U.S.A.)

Crop	*Yield*	*N*	P_2O_5	K_2O
		Kilograms per hectare		
Alfalfa	3.600	82	18	82
Brome grass	1.800	18	7	28
Coastal Bermuda	7.200	82	32	123
Red clover	1.800	45	7	36
Maize: grain	2.700	41	16	11
stover	2.700	28	11	43
Cotton: lint	230	0.6	0.2	1
seed	460	16	7	7
Plants	920	18	7	11
Grasses	1.800	18	9	28
Lespedeza	1.800	36	9	18
Oats: grain	1.200	22	9	7
straw	1.800	11	4	32
Peanut (groundnuts): nuts	900	28	7	9
Vines	1.800	36	4	36
Potatoes, Irish: tubers	10.800	36	14	66
tops	—	28	4	25
Potatoes sweet: roots	5.400	14	9	32
vines	900	18	4	16
Sorghum: grain	—	22	11	7
fodder	1.800	18	7	28
Soybeans: beans	2.200	66	16	25
hay	1.800	41	11	36
Tobacco: leaves	700	18	3	18
stalks	700	9	2	9
Wheat: grain	2.200	22	11	7
straw	1.800	9	3	18

Sources: S. L. Tisdale and W. T. Nelson. Fundamentals of fertilizer application, soil fertility and fertilizers, p. 319-353. New York, Macmillan, 1958.

[State of Food & Agriculture 1963, (F.A.O., Rome), 1963, 142]

TABLE 2—EFFECT OF FERTILIZER ON YIELDS OF SELECTED CROPS

	Crop	*Duration of experiment*	*Fertilizer* $(N+P_2O_5+K_2O)$	*Yield/ha on checks*	*Yield/ha on fertilizer*	*Per cent increase*
		Years	*Kg/ha*	*Kilograms*		%
India	Tea	10	135	591	1 134	92
Germany, Fed. Rep.	Hay	10	240	3 560	8 740	146
India	Tapioca	1	370	8 510	25 310	197
Tanganyika	Pigeon pea	1	210 (+manure)	581	1 840	217
United States	Wheat	4	200	659	2 285	247
Puerto Rico	Sugar cane	5	400	9 856	41 216	318

[State of Food & Agriculture 1963, (F.A.O., Rome), 1963, 140]

TABLE 3—FERTILIZER CONSUMPTION PER CAPITA (1962-63)

(*Kilogrammes*)

Continent/country	N	P_2O_5	K_2O	*Total*
1	2	3	4	5
Europe	11.38	11.17	11.28	33.83
Austria	9.01	13.48	27.16	49.65
Belgium	11.82	12.47	20.02	44.31
Czechoslovakia*	10.55	11.48	13.78	35.81
Denmark	30.92	24.50	37.69	93.11
Finland	17.87	17.38	13.23	48.48
France	14.53	22.00	19.36	55.89
Germany East*	14.81	12.32	27.26	54.39
Germany West	13.49	12.42	19.32	45.23
Italy	7.48	7.50	2.65	17.63
Netherlands	24.92	8.60	10.51	44.03
Norway	15.14	12.15	14.84	42.13
Poland*	9.87	7.72	11.84	29.43
Spain	11.21	10.10	3.10	24.41
Sweden	14.98	13.62	11.50	40.10
United Kingdom	10.12	8.10	8.31	26.53
U.S.S.R.	4.83	3.85	3.73	12.41
North & Central America	13.38	10.99	8.61	32.98
Canada*	5.28	10.58	5.73	21.59
U.S.A.	18.40	14.56	11.69	44.65
South America	1.37	1.44	0.85	3.66
Chile	4.14	6.51	1.27	11.92
Peru	6.17	2.87	0.79	9.83
Asia	1.77	0.83	0.67	3.27
Ceylon	3.83	0.13	2.91	6.87
China Taiwan	9.81	2.67	2.10	14.58
India	0.94	0.20	0.09	1.23
Israel	8.42	5.06	1.00	14.48
Japan	7.05	4.90	5.33	17.28
Korea Rep. of*	8.31	3.14	0.66	12.11
Pakistan	0.64	0.11	0.06	0.81
Phillippines	1.64	0.85	1.10	3.59
Africa	1.48	1.15	0.37	3.00
South Africa	4.25	9.04	2.34	15.63
U.A.R.*	7.03	1.77	0.12	8.92
Oceania	3.03	53.94	5.45	62.42
Australia	3.47	60.60	3.56	67.63
New Zealand	2.50	96.46	20.60	119.56
World**	5.05	4.56	3.77	13.38

* Figures refer to the year 1961-62.

** Excluding Mainland China.

Source: Calculated from FAO Year Book—1963.

[Fertilizer Statistics 1963-64, (Fert. Assn of India, New Delhi) 1965, 197]

TABLE 4—RATIO OF P_2O_5 AND K_2O CONSUMPTION TO N CONSUMPTION

	P_2O_5			K_2O		
	1937-38	1949-50	1960-61	1937-38	1949-50	1960-61
Europe	1.72	1.36	1.06	1.53	1.32	1.07
U.S.S.R.	1.58[1]	1.44[2]	1.07[3]	1.35[1]	1.37′	1.00[2]
North America	2.10	2.04	0.90	1.29	1.11	0.73
Latin America	0.54	1.11	0.64	0.61	0.44	0.57
Near East	0.15	0.27	0.33	0.04	—	0.04
Far East	0.68	0.57	0.45	0.32	0.25	0.48
Africa	3.85	4.33	1.69	0.68	1.00	0.69
Oceania	22.41	24.00	26.67	1.13	0.50	3.33
World	1.71	1.55	0.96	1.15	1.05	0.83

[1] 1940
[2] 1950
[3] 1960

[State of Food & Agriculture 1963, (F.A.O., Rome), 1963, 137]

TABLE 5—ESTIMATES OF ADDITIONAL OUTPUT OF AGRICULTURAL COMMODITIES BY MAJOR INPUTS, INDIA: 1965-66 TO 1970-71

(Million tonnes)

Sl. No.	Crops	Production in 1965-66	Area and irrigation: Unirrigated area	Irrigated area	Total area	Total irrigation	Aggregate	Improved seeds	Fertilizers	Other inputs	Total additional output	Total output target in 1970-71
1	2	3	4	5	6	7	8	9	10	11	12	13
1.	Rice ..	38.05	−2.62	4.47	0.21	1.64	1.85	1.79	2.82	2.77	9.23	47.28
2.	Wheat ..	12.20	0.49	1.55	1.39	0.65	2.04	1.07	3.06	2.65	8.82	21.02
3.	Other cereals ..	25.75	−3.47	−0.26	−3.64	−0.09	−3.73	1.10	4.44	0.78	2.59	28.34
4.	Cereals ..	76.00	−5.60	5.76	−2.04	2.20	0.16	3.96	10.32	6.20	20.64	96.64
5.	Pulses ..	14.07	0.93	0.39	1.18	0.14	1.32	1.56	2.36	2.24	7.48	21.55
6.	Foodgrains ..	90.07	−4.67	6.15	−0.86	2.34	1.48	5.52	12.68	8.44	28.12	118.19
7.	Groundnut ..	5.01	0.15	0.22	0.30	0.07	0.37	0.45	0.19	0.25	1.26	6.27
8.	Cotton* ..	6.34	0.09	0.98	0.50	0.57	1.07	0.22	0.34	0.92	3.05	9.39
9.	Sugarcane† ..	110.00	0.20	20.97	10.90	10.27	21.17	4.30	6.21	3.52	35.2	145.2

* In million bales.
† In terms of cane.

[*A Strategy for the IV Plan*, (Nat. Coun. Appl. Econ. Res., New Delhi), 1964, 37]

TABLE 6—ESTIMATES OF CONSUMPTION OF CEREALS IN INDIA 1965-66 AND 1970-71

(Million tonnes)

	Output (1965-66)	*Human consumption* (1965-66) (a)	*Percentage*	*Output* (1970-71)	*Human consumption* (1970-71)	*Percentage*
Rice	38.0	35.1	44.5 (43.1)	47.3	44.6	43.2
Wheat	12.2	10.7	13.6 (17.5)	21.0	19.0	18.4
Other cereals	25.7	22.6	28.7 (27.0)	28.3	24.2	23.4
Pulses	14.1	10.4	13.2 (12.4)	21.6	15.4	14.9
Total	90.0	78.8	100.0	118.2	103.2	100.0

(a) The figures for human consumption of rice and wheat do not include imports. If imports of about 1 million tonnes of rice and 4 million tonnes of wheat are added the proportion of consumption of each item will vary and is shown within brackets in the next column. The comparison of 1970-71 figures i made with these proportions.

[*A Strategy for the IV Plan*, (Nat. Coun. Appl. Econ. Res., New Delhi), 1964, 32]

TABLE 7—WORLD POTASH PRODUCTION

('000 *tonnes* K_2O)

	1963	1964
Canada	569	782
Chile	18e	19e
France	1,671	1,748
East Germany	1,845	1,857
West Germany	1,948	2,201
Israel	102	152
Italy	114	128
Spain	260	292
U.S.A.	2,603	2,722
U.S.S.R.	1,414	1,684
Other Europe	3	3
Total	10,547	11,588

[Phosphorus & Potassium, No. 7, (1965), 26]

TABLE 8—CONSUMPTION OF FERTILIZERS PER UNIT AREA DURING 1962-63

Name of the Country	*Consumption of fertilizer in kg per hectare*
Japan	233.59
Netherlands	225.56
Belgium	241.07
West Germany	181.62
United Kingdom	71.85
France	76.08
United Arab Republic	94.83
Italy	42.83
United States of America	18.88
India	3.17

[Japan Urea Centre News, Oct. 1965]